Local distribution of deep centers in GaP studied by infrared cathodoluminescence

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Near-infrared cathodoluminescence (CL) in the scanning electron microscope has been used to characterize GaP:S. Spectra of as-grown crystals show a broadband at about 1240 nm, probably related to P_{Ga} antisite defects. This emission has been found to be higher at dislocations giving a CL image opposite to the visible CL image.

Due to the use of GaP in the field of light-emitting diodes, its visible luminescence, with bands in the green and red spectral regions, has been often investigated. One of the techniques used was cathodoluminescence (CL) in the scanning electron microscope which provides information about the spatial distribution of the recombination centers. On the other side deep recombination centers in GaP, emitting in the near infrared (NIR) have been studied by photoluminescence and optical detected magnetic resonance (OMDR)[1-4] and several models to explain the appearance of luminescence bands in the range 1000–1300 nm have been given. As in the case of visible luminescence, space-resolved CL techniques could give additional information on the defects involved in the NIR emission. However, to our knowledge, such techniques have not been applied to the study of deep centers in GaP. In the present work NIR CL in the scanning electron microscope has been used to study the nature and distribution of radiative centers in liquid-encapsulated Czochralski (LEC) GaP:S.

The samples used were cut from a ⟨100⟩ oriented S-doped LEC GaP wafer with a free-carrier concentration n of $3\text{–}4\times10^{17}$ cm^{-3}. The samples were observed in the emissive and CL modes in a Hitachi S-2500 or a Cambridge S4-10 scanning electron microscope at an accelerating voltage of 30 keV and beam currents of 10^{-7}–10^{-6} A. For the obtention of panchromatic NIR CL images an optical lens was used to concentrate the light on a cooled North Coast EO-817 germanium detector attached to a window of the microscope. In some cases CL images for wavelengths above 1000 nm were recorded by adapting a cut-on optical filter at the detector entrance. To record spectra a light guide feeding the light to an Oriel 78215 computer-controlled monochromator was used. In cases of low signals, spectra representing the average of a high number of measurements are readily obtained. The spectra, covering the range 800–1800 nm, were corrected to include the system spectral response. Due to the low emission at room temperature, all CL measurements were carried out at 170 K. Besides as-grown samples, samples which had received the following treatments were investigated: (a) annealing in argon atmosphere at 1000 K for times ranging from 1 to 5 h, (b) irradiation with 2.8 MeV electrons to a dose of 8×10^{18} e^- cm^{-2}, (c) electron irradiation, as in (b), followed by annealings at 700 and 930 K for 1 h. Visible CL of the same samples used in this work has been previously investigated.[5-7]

Figure 1(a) shows the CL spectrum of an as-grown sample with a broad (full width at half maximum of 360 nm) band centered at about 1240 nm (1.0 eV). This spectrum has been recorded under the normal observation conditions of the scanning electron microscopy, with the electron beam focused on the sample. With a defocused beam the spectrum of Fig. 1(b) showing the tail of an intense red band and a composite broad IR band with a peak at about 1320 nm (0.94 eV) is recorded.

The 1240 nm band (obtained with focused beam) is strongly reduced by annealing as-grown samples above 830 K. Annealing the as-grown samples at 1000 K for 1 h induces only minor changes in the spectra obtained with a defocused beam. The spectra show a small emission peak at 1100 nm (1.13 eV) that increases with annealing time. After 5 h annealing at 1000 K, the spectrum of Fig. 2 is obtained. No spectra could be recorded with a focused beam. In the electron-irradiated samples, the NIR luminescence appears to be quenched, as previously reported for the visible range.[6] Partial recovery of the emission is observed after annealing at 700 K and luminescence further increases by annealing at 920 K for 1 h. The spectrum recorded after this treatment is shown in Fig. 3.

As described above, only the spectra of as-grown samples could be recorded when a focused beam is used. In all other cases the beam has to be defocused to get enough emission to record spectra. Consequently, NIR CL images were obtained only from the as-grown crystals. Figure

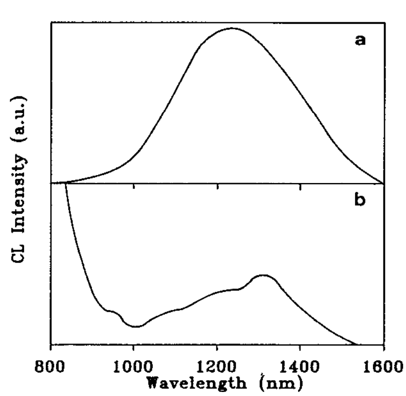

FIG. 1. NIR CL spectra from as-grown samples with (a) focused electron beam and (b) defocused beam.

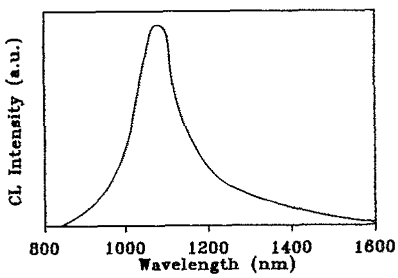

FIG. 2. NIR CL spectrum (defocused beam) of a sample annealed at 1000 K for 5 h.

4(a) shows a representative CL image obtained by using an optical filter transmitting wavelengths above 1000 nm. The corresponding image of visible CL with dot and halo contrast associated with the presence of dislocations[5] is shown in Fig. 4(b). Comparison of both figures reveals that contrast in the NIR CL image is about inverse to that of the visible CL. Most of the dark dislocation points in Fig. 4(b) appear bright in Fig. 4(a).

An infrared band very close to the 1240 nm band observed in this work in as-grown crystals has been previously reported. Killoran *et al.*[1] concluded from their ODMR experiments that P_{Ga} antisite takes part in an electron capture process which competes with the visible photoluminescence emission. In particular, they assign emissions at 1130 nm (1.1 eV) and 1275 nm (0.97 eV) to different recombination processes involving the P_{Ga} antisite. Yang *et al.*[2] have also detected the 1275 nm emission and have related it to the presence of P_{Ga}. We suggest that the NIR band of our as-grown crystals is the antisite-related band of Refs. 1 and 2. Since in these crystals only one band is observed in the NIR region, the CL image would provide information about the P_{Ga} defect distribution in the sample, in particular around dislocations. The CL images indicate that the NIR emitting centers concentrate near the dislocation core and other crystal regions, leaving a denuded zone around dislocations. The fact that the 1240 nm band disappears by annealing would be a consequence of the annealing out of antisite defects. In GaAs, thermal annealing of As_{Ga} has been found to start at 780 K,[8] which is about the temperature causing a significant reduction of the 1240 nm band in this work. On the other hand, annealing the as-grown samples causes the appearance of the 1100 nm band shown in Fig. 2. Since such thermal treatment causes a selective loss of phosphorus,[9] vacancies in the P sublattice would be involved in the emerging band. In Ref. 2, V_P have been also related to a 1100 nm luminescence band.

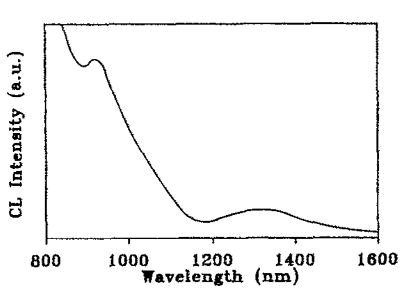

FIG. 3. NIR CL spectrum (defocused beam) of a sample irradiated and annealed at 925 K.

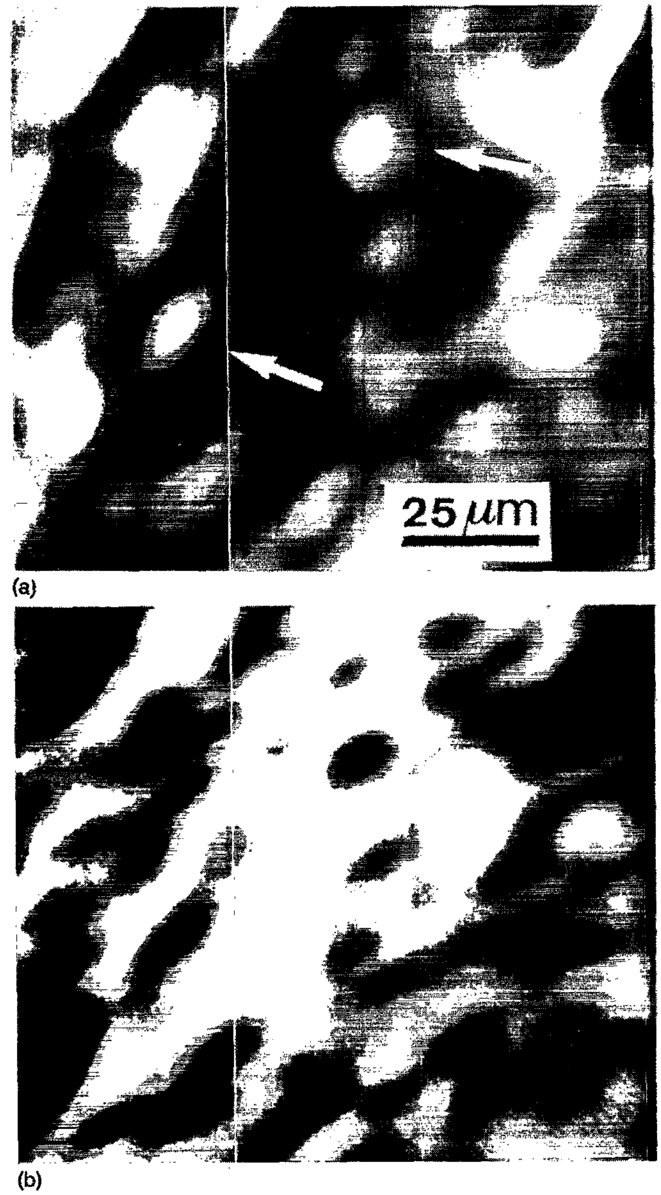

FIG. 4. (a) NIR (wavelength above 1000 nm) and (b) visible CL images of the same area of an as-grown sample. Arrows indicate two emergence points of dislocations.

The quenching of NIR-CL by high-energy electron irradiation has been also found in the visible spectral range.[6] An irradiation experiment was aimed to check if radiation-induced defects act as recombination centers in the infrared region quenching the visible luminescence. The results indicate that irradiation creates mainly nonradiative recombination centers quenching both the visible and NIR luminescence.

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