

Spatial distribution of Mn-related emission in GaP studied by cathodoluminescence and photoluminescence

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Abstract

Cathodoluminescence (CL) from untreated as well as heat-treated GaP:Te:Mn samples has been investigated. Spectra of untreated samples present two emission bands that peak at 585 and 730 nm. The CL image shows bright spots associated with dislocations, as well as doping striations. The red band (730 nm) is higher at these bright spots. Heat treatments enhance the red-band emission, while the bright spot contrast remains. Time-resolved photoluminescence indicates that the red band is due to excitons bound to complexes.

Introduction

The growing interest in III-V compounds has rendered it important to know the effect of transition metals on their physical properties. GaP is the only III-V material where Mn originates a deep centre due to Mn^{2+} . The luminescence of this centre occurs in the near infrared, with two temperature-dependent zero-phonon lines at 1.534 and 1.5354 eV due to the ${}^4T_1 \rightarrow {}^6A_1$ transition [1]. Photoluminescence (PL) of Mn-doped n-type GaP, in particular GaP:Te:Mn, has been found to be different from that observed in as-grown and heat-treated GaP:Te samples. PL spectra of Mn-doped samples show a drastic decrease in Te-C recombination luminescence and the appearance of two bands peaked at 730 nm (band M) and 860 nm (band N), respectively, while intra-ionic Mn^{2+} recombination is not observed [2]. In the present work the nature of the 730 nm band is investigated.

Experimental

Cathodoluminescence (CL) in a scanning electron microscope is used to investigate the recombination processes associated with the 730 nm band in GaP:Te:Mn and their possible spatial distribution. The same set of GaP:Te:Mn samples was studied by steady-state and time-resolved PL. CL measurements were performed in a Hitachi S-2500 SEM at room temperature. The experimental arrangement for CL obser-

vations has been described elsewhere [3]. PL was excited by the 514.5 nm Ar ion laser line (steady state) or a pulsed Xe arc (time resolved). The experimental arrangement has been described previously [4]. The changes in CL emission produced by annealing treatments at 1300 K during 0.5 h and 7 h, respectively, in inert atmosphere have also been studied.

Results and discussion

CL spectra of n-type GaP crystals have been described often. Under a wide range of experimental conditions the visible spectrum consists of a broad band centred at about 560 nm, which corresponds to the near band edge emission. This band has been reported in, for instance, GaP:Te [5] and GaP:S [6]. In some cases a band at 610 nm, attributed to centres involving donors and Ga vacancies, is also observed [5, 7]. In ref. 7 the conditions for the appearance of the 610 nm emission have been described.

Figure 1 shows the CL spectrum of the unannealed GaP:Te:Mn samples used in this work, with two bands centred at 585 and 730 nm. The 585 nm band is probably composed of the 560 and 610 nm bands, while the 730 nm band corresponds to the above-mentioned M band. The typical CL spectra of n-type GaP without Mn doping shows a similar green emission and the absence of the 730 nm luminescence [5, 6]. The total CL image (Fig. 2) shows bright spots and lines, revealing the

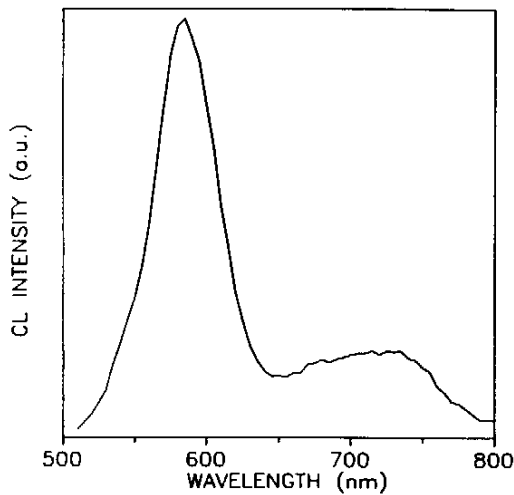
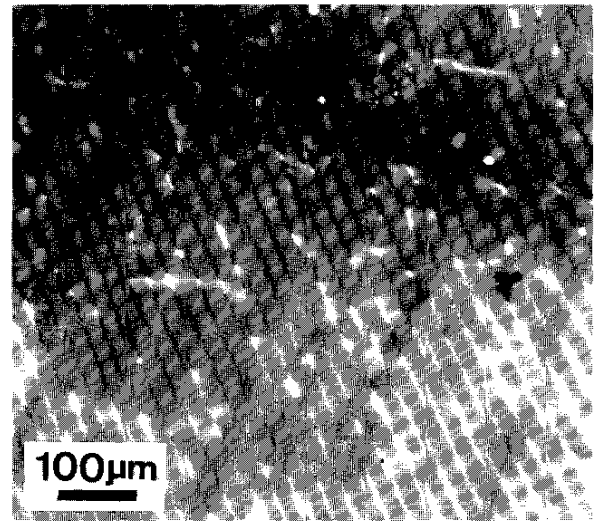


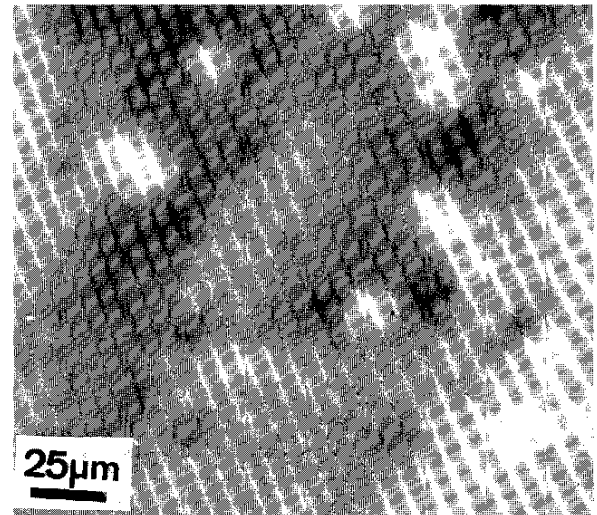
Fig. 1. Spectrum of the unannealed GaP:Te:Mn sample.

typical dislocation distribution as well as doping striations. An analysis of the relative intensity of both bands inside and outside the bright spots shows that the relative contribution of the red (730 nm) band is higher at the dislocations. The dislocation contrast disappears in the images obtained with a 590 nm band-pass filter. This result agrees with the above-mentioned PL observations if the bright spots in the total CL image are due to the contribution of the red (730 nm) band generated by Mn-related complexes which are concentrated mainly at dislocations. Although red CL emission in the 700 nm region has previously been reported in GaP [6], no spatial inhomogeneity was reported. Contrary to the present results, the CL red band can usually be revealed in the spectra obtained in the SEM only when a defocused electron beam is used. The Mn-related enhancement of the 730 nm emission enables the recording of CL images providing information on the spatial distribution of the complexes.

Annealing of GaP:Te:Mn samples for 0.5 h at 1300 K causes an increase in emission in the red spectral region, as Fig. 3 shows. In addition, the above-mentioned 610 nm band is present, although it appears to peak at 630 nm owing to the contribution of the red band. This increase could be due to aggregation processes of the Mn-related defects during thermal treatment. CL images of annealed samples do not show significant changes in the bright spots and present the same qualitative contrast as in Fig. 2. A further annealing for 7 h at the same temperature causes an enhancement of the 610–630 nm emission relative to the red band. The 610–630 nm band, which increases with annealing treatments, is attributed to donor–Ga vacancy complexes [5, 7]. This indicates the stability of defects and complexes around dislocations up to 1300 K.



(a)



(b)

Fig. 2. (a) Total CL image of the unannealed GaP:Te:Mn sample; (b) the same region at higher magnification.

The photoluminescence studies for the above band-gap excitation indicate that the emission with a maximum at 570 nm is weaker than the red emission, even for the unannealed sample. A detailed study of the band M as a function of temperature by time-resolved spectroscopy indicates that it is the superposition of two emissions, one with a maximum at 715 nm (1.735 eV) and a decay time of 0.8 ms (band M_1) and the other with a maximum at 756 nm (1.64 eV) and a decay time of 10.8 ms (band M_2), as shown in Fig. 4 for 11 K.

Steady-state spectra can be adjusted to the sum of these two emissions, up to 90 K. The intensity de-

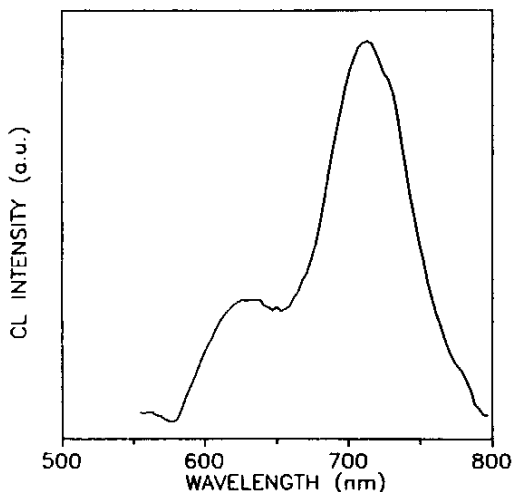


Fig. 3. Spectrum of the GaP:Te:Mn sample after annealing at 1300 K for 0.5 h.

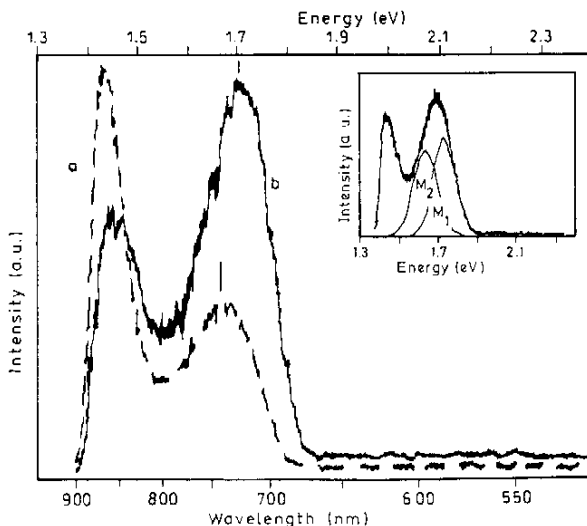


Fig. 4. Time-resolved spectra of GaP:Te:Mn at 11 K viewed between (a) 5 and 20 ms and (b) 0.1 and 0.5 ms. Inset: steady-state spectrum with fit to two gaussians with maxima at 1.735 eV (M_1) and 1.64 eV (M_2).

pendence with temperature closely follows the decay decrease, indicating that the two emissions are thermally quenched, although at different temperatures. At higher temperatures only band M_1 is present. This fact explains the shift toward higher energies observed under steady-state conditions upon increasing temperature. Figure 5 shows the temperature dependence of the decays.

Band N shows a typical donor-acceptor pair recombination behaviour. Although ESR has shown the characteristic spectrum of Mn^{2+} , it has been impossible to detect the known intra-ionic emission of Mn^{2+} superimposed on the pair emission. This may be due to the

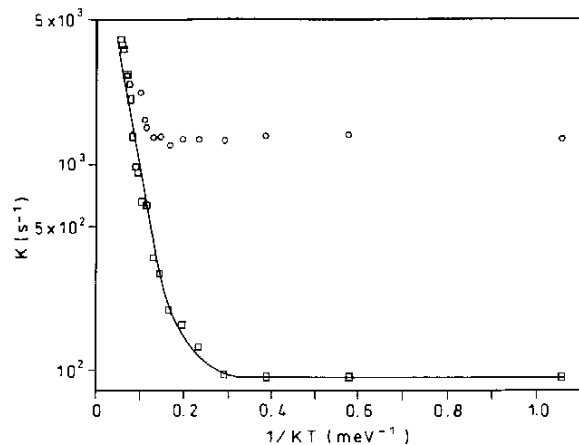


Fig. 5. Temperature dependence of $1/\tau$ of the (O) M_1 and (\square) M_2 bands. The full line is the fit to the experimental $1/\tau$ of the M_2 band, in agreement with $K_{exp} = K_{rad} + K_{nr}$ with $K_{rad} = 92.5 \text{ s}^{-1}$ and $K_{nr} = 1.3 \times 10^4 \exp(-28/kT)$.

fact that other, more efficient paths for the capture of electrons and holes exist or that Mn^{2+} emission is quenched by energy transfer.

The anneal for 7 h causes a decrease in PL, although there are no marked changes in the band shape.

Conclusions

The doping by Mn of GaP:Te samples produces bright spots, with emission with a maximum at 730 nm associated with dislocations in the CL image. Time-resolved spectra show that this emission is due to excitons bound to complexes, while the intra-ionic Mn^{2+} luminescence is absent.

Acknowledgements

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