Spatial distribution of vacancy defects in GaP wafers

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(Received 5 August 1987; accepted for publication 13 November 1987)

Cathodoluminescence scanning electron microscopy and positron annihilation techniques have been used to investigate the distribution of defects in GaP wafers. The results show the existence of a gradient of the concentration of vacancy-type defects along the wafer diameter, which causes inhomogeneity in the emission. Dislocation density and vacancy concentration profiles have been compared.

INTRODUCTION

The spatial distribution of defects in wafers of III-V semiconductors is of great interest in semiconductor technology and has been previously studied by different methods such as infrared absorption, x-ray topography, cathodoluminescence (CL) in the scanning electron microscope, etc. Many of these previous works refer to GaAs while less information is available on GaP and other materials. The CL image of GaP often shows dislocations surrounded by a bright halo (dot and halo contrast). It has been suggested that this effect is due to the diffusion of vacancies or other point defects, which act as nonradiative recombination centers, to the dislocations.[1-3] For this reason, dislocations can influence the space distribution of the green band-edge luminescence, at about 563 nm, and a deep-level band centered at about 732 nm. In the present work the CL technique has been used to characterize the uniformity of GaP:S wafers by measuring the dislocation density and the intensities of both luminescence bands along the wafer diameter. On the other hand, positron annihilation measurements have been performed in order to investigate the distribution of vacancies along the wafer and the possible influence of the vacancies on the observed luminescence variations.

EXPERIMENTAL METHODS

The sample used in this study was a ⟨100⟩ oriented S-doped LEC-GaP wafer with 50 mm diam and a free-carrier concentration n of $3–4\times10^{17}$ cm^{-3}. Most of the measurements were done on a 5-mm-wide strip, containing the center of the wafer, which was cut with a diamond saw along a wafer diameter. Preliminary CL and etching observations were done on samples cut from other wafer regions. For the chemical etching the solution of H_2SO_4, H_2O_2, and HF with volume parts 3:2:2, described in Ref. 4 was used. The samples were etched for 2 min at 70 °C. The samples were observed in a Cambridge S4-10 scanning electron microscope at 30 kV, at room temperature, in the emissive and CL modes. The experimental method for CL measurements, in the range of 350–850 nm has been previously described.[5] For the observations in the SEM, the strip was cut in ten parts (of about 5×5 mm^2 each) which were placed in a single specimen holder in order to perform the CL measurements under the same experimental conditions. This set of samples was also used for positron annihilation measurements.

To form a sandwich configuration for the positron measurements, a reference sample cut from the same wafer was moved along the wafer diameter together with the source in 5-mm steps. The positron source was prepared by evaporating a ^{22}NaCl solution onto a nickel foil (1.2 mg cm^{-2}). The lifetime measurements were made by using a conventional coincidence system having a time resolution of 320 ps (FWHM). After subtracting the source contribution (11% of 180 ps for Ni and 3.5% of 500 ps for salt) one-component decomposition gave satisfactory fits.

RESULTS

Figure 1(a) shows the surface of an etched sample. Some larger pits are observed on a background of smaller and shallow pits. Both kind of pits have the same appearance than the dislocation (D) and saucer (S) etch pits, respectively, which have been previously[6,7] described. Figure 1(b) shows the total CL image of the area shown in Fig. 1(a). The dot and halo contrast, which has been associated with the presence of dislocations is observed in Fig. 1 only at the points where larger pits appear in the emissive mode image. The same CL contrast is observed in polished unetched samples. For these reasons we assumed that the dot and halo images represent dislocations and used the CL to measure the dislocation density along the wafer diameter. Figure 2 shows the dislocation density profile obtained.

The CL images obtained by using different optical filters show that the emission from halos is mainly green. Figure

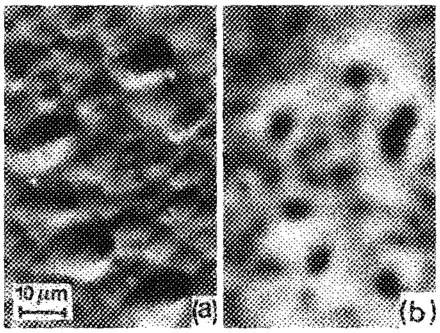

FIG. 1. Image of an etched sample in the scanning electron microscope (a) emissive mode, (b) cathodoluminescence mode.

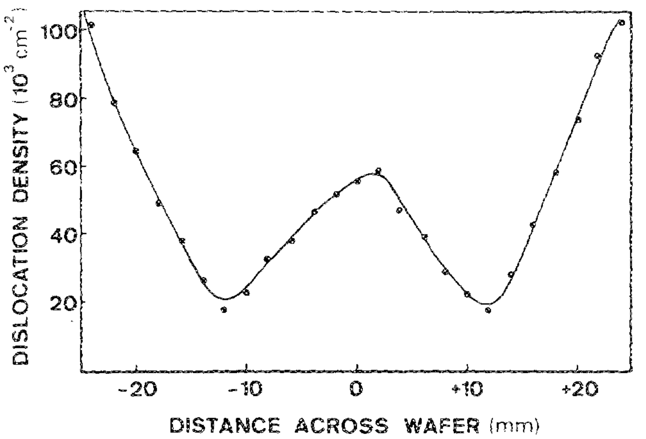

FIG. 2. Dislocation density across the wafer diameter.

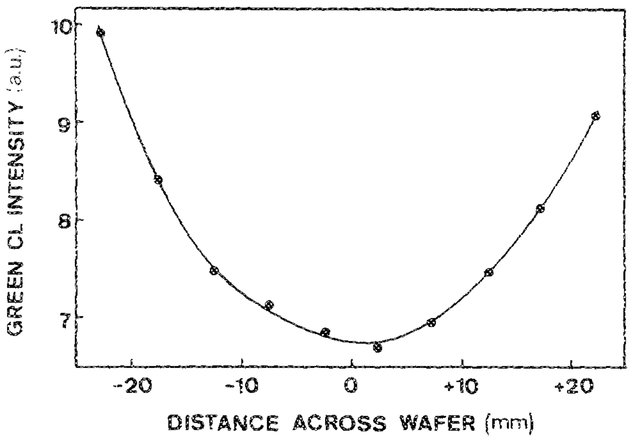

FIG. 4. Profile of the green-band-edge luminescence across the wafer diameter.

3(a) shows a representative CL spectrum of the samples, with a green band centered at about 563 nm. This spectrum has been recorded under the normal observation conditions of the SEM, with the electron beam focused on the sample. With a defocused beam the spectrum of Fig. 3(b), showing a red band in 732 nm, is recorded. No spectral variations are observed along the wafer diameter but the intensities of the green and red bands exhibit profiles shown in Figs. 4 and 5, respectively. The mean lifetime of positrons also varies along the wafer diameter as Fig. 6 shows.

DISCUSSION

The presence of halos surrounding the dislocations in the CL images of GaP has been explained by point defect diffusion to the dislocations. Frank and Gösele,[3] by discussing experimental work[1,2,8,9] on luminescence of GaP, point out that recombinations involving vacancies compete with green-band transitions and therefore the green-band intensity decreases when the vacancy concentration increases. If the vacancies are removed by diffusion to dislocations, the green emission is enhanced in the vacancy-poor region surrounding the dislocation. The formation of halos would explain[3] the increase of photoluminescence and cathodoluminescence observed in Ref. 8 during irradiation with laser or electrons, respectively. The regions with a higher density of dislocations with halos would have a lower vacancy concentration and consequently higher green-luminescence emission. The dislocation density profile is W shaped as Fig. 2 shows. Such profile has been previously observed in GaP[10] and GaAs (Refs. 11 and 12) LEC wafers. The green-luminescence profile in the wafer is U shaped, as shown in Fig. 4. This observation partly disagrees with the above-mentioned model. Although at some distance from the center of the wafer there is a good correspondence between dislocation density and green luminescence the central peak of the dislocation density profile does not have a counterpart in the green-luminescence profile. The CL images from different parts of the wafer show that in the central region the dislocation halos are less intense than the halos in the edge. This effect, possibly related to the point defects distribution which results from the growing method, causes that the luminescence profile does not show a central peak. On the contrary, a good correspondence between the W-shaped profile of the dislocation etch pits density and the profiles of different luminescence bands was found in GaAs.[11]

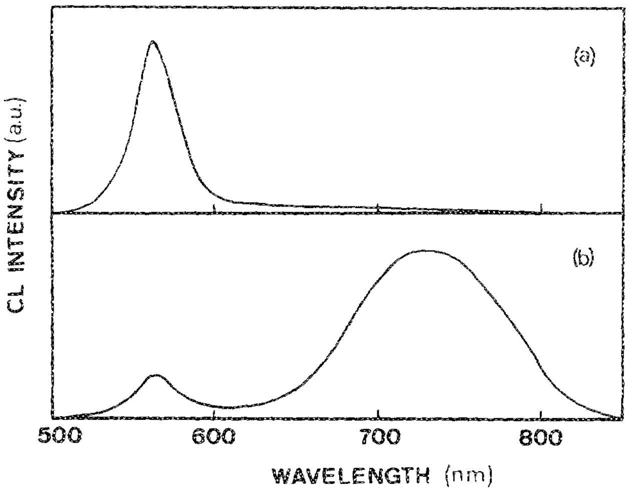

FIG. 3. CL spectra at room temperature. (a) Focused beam; (b) defocused beam.

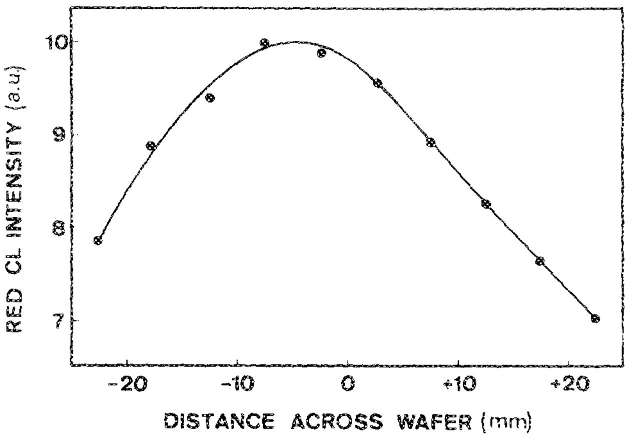

FIG. 5. Profile of the red deep level band luminescence across the wafer diameter.

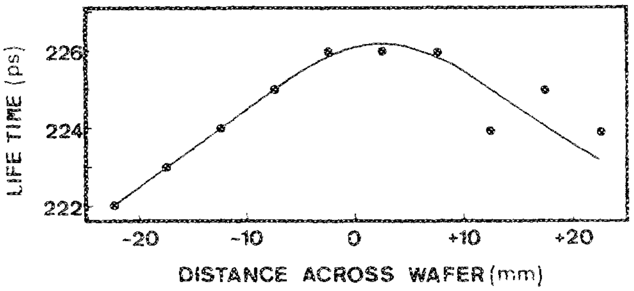

FIG. 6. Positron lifetime across the wafer diameter. The absolute error is 1.5 ps.

If, as assumed, the vacancies act as competitors of the green band, the profile of the vacancy concentration along the wafer diameter should be the inverse of the green-luminescence profile (Fig. 4). This is in fact deduced from Fig. 6 which shows the positron annihilation results. The mean positron lifetime (solid line) is influenced by the presence of neutral or negatively charged defects which cause the positron trapping. Positively charged defects repel positrons. The positron annihilation technique detects mainly vacancy-type defects. Dislocations are detected only when the density is above 10^8 dislocations per cm^2 [13] while antisite defects, neutral impurities, and interstitials are not expected to influence the positron lifetime. Since the maximum dislocation density in the wafer is about 10^5 dislocations per cm^2, the variations of positron lifetime along the wafer can be attributed to vacancy-type defects. Dlubek, Brümmer, and Polity[14] have used positron lifetime measurements to study vacancy defects in n-type GaP. They obtain a bulk value for free positrons of 223 ± 2 ps and a trapped positron lifetime of 290 ± 10 ps. From comparison with previous positron lifetime measurements in GaAs,[15] they conclude that the defects trapping positrons in their S-doped GaP crystals are vacancies in the P sublattice. Figure 6 shows the existence of a slight variation of τ along the wafer with values slightly higher than the mentioned bulk value and a maximum in the center of the wafer. In this region the vacancy concentration would be somewhat higher than $5 \times 10^{16}\ \mathrm{cm}^{-3}$, which is the detection limit of the positron method.[15] Although the τ variations are small, these agree well with the green CL results (Fig. 4) and we suggest that they really represent variations of the vacancy concentration.

The red CL profile (Fig. 5) has the shape of the positron lifetime profile and is therefore the inverse of the green CL profile. Tajima, Okada, and Tokumaru,[1] in a study of CL from dislocations in S-doped LEC GaP found a complementary contrast of the two main bands. The green-band intensity decreases at the center of dislocation pits while the red-band intensity increases in the same region. Such contrast, at a more macroscopic scale, is represented in this work by Figs. 4 and 5, and can be explained if vacancies, besides quenching the green luminescence, form centers, probably a vacancy-donor complex[1,16] associated with the red emission at about 710–720 nm. The similarity of the positron lifetime and red CL profiles support this possibility although the red emission has been also assigned[3] to interstitials or/and antisite defects. The nature of the vacancy-type defects, whose concentration gradient has been detected in the present work, is not well determined. As mentioned above, Dlubek, and co-workers[14] attributed their positron lifetime results in GaP to the presence of P vacancies, either isolated or forming complexes with antisites or impurities, but the luminescence data, reviewed in Ref. 3 indicate that both P and Ga vacancies act as strong green-band competitors.

ACKNOWLEDGMENTS

The authors thank Wacker-Chemitronic (Dr. K. Löhnert) for providing the samples. The help of P. Fernández is acknowledged.

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