

## Photoluminescence at Dislocations in GaAs

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Photoluminescence measurements with high spatial and spectral resolution on *n*-type GaAs at helium temperatures show the reduction of radiative quantum efficiency immediately at individual deformation-induced dislocations to be orders of magnitude stronger than near grown-in dislocations.

Dislocations in semiconductors can lead to formation of distinct electronic levels and cause inhomogeneities of charge and dopant distributions.<sup>1</sup> Radiative recombination of electron-hole pairs is known to be affected by the presence of dislocations.<sup>2-4</sup> However, the details of the fundamental processes of recombination at and around dislocations are still insufficiently understood. For GaAs, this question has recently become of exceptional importance because the quantum efficiency of injection lasers is degraded by dislocation effects.<sup>5-8</sup>

In this paper we present the first definitive correlations between dislocations and recombination by measuring luminescence spectra directly at and adjacent to individual dislocations of various origin. High spatial resolution on the specimen surface is combined with high spectral resolution at helium temperatures for identification of the specific electronic transitions in *n*-type GaAs.

A special helium cryostat<sup>9</sup> enabled us to position the samples as close as 12 mm to an external microscope illuminator system, which is used to focus light from a He-Ne laser onto the sample for photoluminescence excitation and to collect the recombination radiation for analysis in a grating spectrometer. The cryostat was mounted on a micrometer stage with motion feasible in both coordinates within the plane of the sample surface. A spatial definition of better than  $\pm 3 \mu\text{m}$  was achieved.

The excitation intensity was kept low to avoid disturbances. Less than 0.8 mW of the 1.96-eV laser radiation impinged on the sample. We convinced ourselves of the independence of our results upon excitation level by inserting a series of neutral-density filters. Sample temperature during excitation was approximately 10 K.

The samples to be discussed here were *n*-type

GaAs, Se-doped, with room-temperature electron concentrations between  $(3 \text{ and } 4) \times 10^{17} \text{ cm}^{-3}$ . Electron mobility at room temperature was typically  $3300 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ . We estimate the compensation to be of the order of 20%, mostly due to silicon acceptors. The surfaces, of (100) orientation, could be etched after the luminescence was taken in order to correlate the details of the spectra with dislocation etch-pit distributions or dopant striations.<sup>10</sup>

We investigated both as-grown dislocations and fresh dislocations introduced by a controlled plastic deformation. This deformation was done in a protective atmosphere of forming gas by applying a constant load of 8.1 kg in the direction of a  $\langle 123 \rangle$  axis at 580°C.<sup>11</sup> This procedure is known to result in well-defined dislocation distributions by predominant glide.<sup>11</sup> The dislocations are mostly<sup>11</sup> of the "60-degree" type.<sup>12</sup> After the deformation the samples were cut to display a (100) surface which was then lapped and polished to yield specimens identical in orientation and surface finish with the undeformed ones. This precaution was taken to avoid problems from non-radiative surface recombination, which is very effective in GaAs.<sup>13</sup> Several series of measurements, including experiments on dopant variation and correlations with etch patterns,<sup>9,10</sup> assured us that our data are not masked by accidental variations of the surface recombination rate but truly represent the bulk and its defect structure.

As-grown dislocations have turned out to be relatively minor perturbations of the recombination processes. By scanning in 5- $\mu\text{m}$  intervals in the vicinity of dislocations we obtained iso-intensity contour maps, an example of which is shown in Fig. 1. Such maps correlate strikingly with details found in high-resolution etch patterns<sup>9,10</sup>; these details will, however, not be discussed

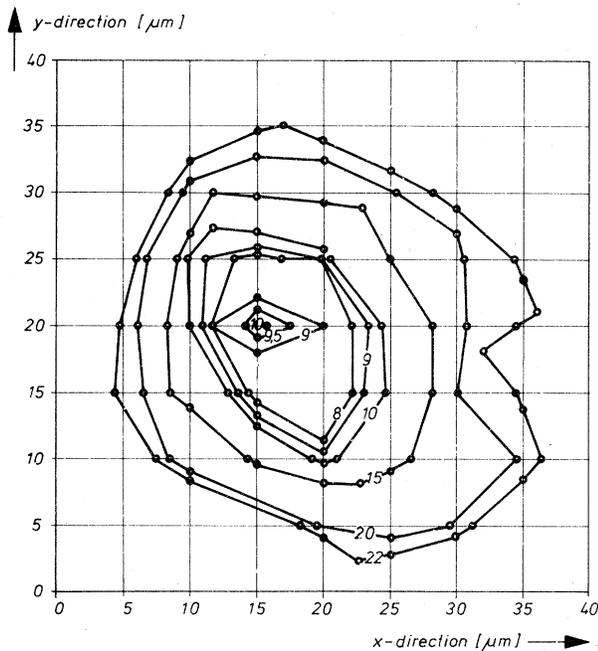


FIG. 1. Typical isointensity luminescence map in the vicinity of a dislocation in GaAs. The numbers indicate the intensity in arbitrary units for the near-gap luminescence at 1.513 eV at helium temperatures.

here. The main results of our studies of these native growth-induced dislocations can be summarized as follows: (i) The near-band-gap recombination (such as donor-to-valence band)<sup>14</sup> is typically reduced by a factor of 2 to 3 within a cylinder of about 20  $\mu\text{m}$  radius around the dislocation, (ii) immediately at the dislocation there is often a recovery (typically 10%) of the intensity of this recombination, (iii) acceptor-related recombination is reduced within the 20- $\mu\text{m}$  cylinder and becomes undetectable at about 5  $\mu\text{m}$  from the core, (iv) the emission resulting from vacancy-impurity complexes<sup>14</sup> indicates no perturbation of the vacancy equilibrium near the dislocation, and finally (v) annealing (up to 20 h at 650°C) does not cause any appreciable changes in the spectra.

All of these results can be explained by the presence of stable Cottrell atmospheres<sup>15</sup> of impurities around the dislocation. It seems likely that acceptors are attracted towards the core and leave a cylinder of acceptor depletion around the dislocation. The relatively small reduction of radiative quantum efficiency is probably caused partly by electric fields, generated by the dopant inhomogeneity, which separate the photocreated

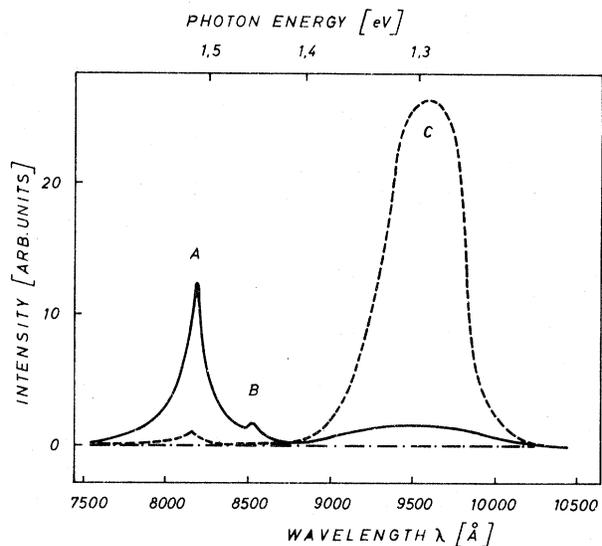


FIG. 2. Photoluminescence spectra of GaAs before deformation (solid curve), after plastic deformation immediately near a dislocation (dash-dotted curve), and after anneal (dashed curve). Band A is caused by donor-to-valence band transitions, B is the phonon replica of a transition involving acceptors, C originates from vacancy-impurity complexes. Spectra are corrected for multiplier response.

carrier pairs, and partly by elastic strains.

Deformation-induced unannealed dislocations exert completely different effects. Immediately at the dislocation there is no more detectable luminescence above our noise level; the luminescence efficiency has dropped by at least 3 orders of magnitude! The extent of this dead zone around the core was measured to be around 5  $\mu\text{m}$  and appears instrument limited; presumably the actual extent is roughly 1 carrier diffusion length, which is somewhat smaller than our resolution. Figure 2 shows that in comparison with undeformed specimens the luminescence has vanished completely throughout the spectrum. We have further extended our measurements with a germanium diode (being less sensitive near 1.5 eV than the usually employed S-1 photomultiplier) down to about 0.8 eV photon energy and did not detect any radiation in this spectral range either. We are thus forced to assume that the core region of a fresh dislocation provides extremely efficient nonradiative recombination centers—such as caused by dangling bonds—or that strong pair-separating electric and elastic fields prevail in the space-charge region surrounding the core.

Apart from the immediate vicinity of the dislo-

cation the sample is only insignificantly changed in its luminescence after deformation. This fact leads to the important and reassuring conclusion that mainly glide-induced dislocations are produced while the point-defect production is negligible, since such production (or any contamination) would have resulted in observable changes of the vacancy-impurity-complex luminescence. Thus all electrical effects observed in samples having undergone similar bending<sup>1,11</sup> can indeed be attributed to dislocations.

Annealing of these deformation-induced dislocations causes drastic changes, as indicated in Fig. 2. A 30-min treatment at 600°C leads to a partial recovery of the near-gap (~1.5 eV) radiative recombination. However, much more dramatic is the qualitative change in the spectrum: The intense band near 1.3 eV indicates dominating vacancy effects. We interpret this result by assuming effective vacancy production through dislocation climb under the annealing conditions. These vacancies associate with donors to form the complexes responsible for the 1.3-eV band.<sup>14</sup> Climb and complexing apparently lead to stable new configurations; any further annealing—even at more elevated temperatures—does not improve the quantum yield nor does it change the spectrum. The recovery of the near-band-gap radiation upon initial anneal suggests saturation of dangling bonds; a rearrangement, as discussed by Hornstra,<sup>12</sup> appears more likely for the relatively low annealing temperature than a bond saturation by impurities.

In conclusion, we have shown with a new high-resolution technique of photoluminescence in the vicinity of individual dislocations that in GaAs only fresh deformation-induced dislocations cause the sharp decline of radiative quantum efficiency. Our method has also been useful in correlating dopant variations with luminescence output and should be generally applicable for such correlations on a microscopic scale, especially for structures resembling optoelectronic solid-state devices where lattice imperfections exert considerable influence.

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ments. We gratefully acknowledge the help of M. Blätte with the samples and of E. Gmelin concerning the cryostat.

<sup>1</sup>H. Alexander and P. Haasen, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1968), Vol. 22, p. 27.

<sup>2</sup>For a review, see H. Mataré, *Defect Electronics in Semiconductors* (Wiley, New York, 1971).

<sup>3</sup>Many experiments were performed on dislocations in the indirect-gap material Ge; see for example A. A. Grippius and V. S. Vavilov, *Fiz. Tverd. Tela* 4, 2426 (1962) [*Sov. Phys. Solid State* 4, 1777 (1963)]; all of these experiments could not resolve the dislocations individually.

<sup>4</sup>GaAs has been investigated by cathodoluminescence; see H. C. Casey, Jr., *J. Electrochem. Soc.* 114, 149 (1967); A. L. Esquivel, W. N. Lin, and D. B. Wittry, *Appl. Phys. Lett.* 22, 414 (1973). These data suffer from the broadness of the room-temperature cathodoluminescence emission.

<sup>5</sup>P. Petroff and R. L. Hartman, *Appl. Phys. Lett.* 23, 469 (1973).

<sup>6</sup>B. C. De Loach, Jr., B. W. Hakki, R. L. Hartman, and L. A. D'Asaro, *Proc. IEEE* 61, 1042 (1973).

<sup>7</sup>W. D. Johnston, Jr., *Appl. Phys. Lett.* 24, 494 (1974).

<sup>8</sup>R. Ito, H. Nakashima, and O. Nakada, *Jpn. J. Appl. Phys.* 13, 1321 (1974).

<sup>9</sup>Details on the apparatus are given by W. Heinke, in *Proceedings of the International Conference on Lattice Defects in Semiconductors*, Freiburg, W. Germany, 22–25 July 1974 (to be published).

<sup>10</sup>Preliminary results on local correlation of luminescence and lattice perfection were reported by W. Heinke, *Verh. Deut. Phys. Ges.* 8, 602 (1974).

<sup>11</sup>R. Labusch and R. Schettler, *Phys. Status Solidi (a)* 9, 455 (1972); more recent references in *Proceedings of the International Conference on Lattice Defects in Semiconductors*, Freiburg, W. Germany, 22–25 July 1974 (to be published).

<sup>12</sup>J. Hornstra, *J. Phys. Chem. Solids* 5, 129 (1958).

<sup>13</sup>J. M. Woodall and H. J. Hovel, *Appl. Phys. Lett.* 21, 379 (1972).

<sup>14</sup>Luminescence of GaAs is reviewed by E. W. Williams and H. B. Bebb, in *Semiconductors and Semimetals*, edited by R. W. Willardson and A. C. Beer (Academic, New York, 1972), Vol. 8.

<sup>15</sup>A. H. Cottrell, *Dislocations and Plastic Flow in Crystals* (Clarendon Press, Oxford, England, 1953), p. 56.