

Fig. 2(b). SOT topograph showing dislocation band in silicon web. [Enlarged section—50 $\times$ —of web crystal shown in Fig. 2(a)].

the strain was lowest, indicating that growth conditions must have been close to ideal.

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## EFFICIENT ELECTROLUMINESCENCE FROM GaAs DIODES AT 300°K\*

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The light-emitting diodes described in this Letter differ from standard type diodes insofar as the amphoteric dopant Si is the dominant impurity on both sides of the junction. The  $p$ - $n$  junction is completely solution regrown. The highly compensated  $p$  region gives rise to a wide active region up to 50  $\mu$  in width. The interesting feature of these diodes is their high external quantum efficiencies at 300°K. Values up to 6% have been measured on diodes, when an antireflecting coat has been applied.

It is a widely adopted procedure to use Zn as the dominant acceptor on the  $p$  side of the junction of GaAs light-emitting diodes.<sup>1</sup> Zn is known to form a very shallow level and the emitted radiation has an energy close to the band gap of GaAs. The active region in which the radiative recombination occurs is generally on the order of a few microns.

The light-emitting diodes, described here, are of a 3-layer structure  $p^+p_0n$ . They differ in the following respects from the standard type diodes:

(1) The  $p$ - $n$  junction is completely solution-grown and amphoterically-doped; that is, the amphoteric dopant Si is the dominant impurity on both sides of the junction. This gives a highly compensated  $p$  region.

(2) The light-emitting region is extremely wide, up to 50  $\mu$ .

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(3) The energy of the emitted light is less than the band-gap energy of GaAs at 300°K.

The most important feature of these diodes is that their external quantum efficiencies are much higher than those of the standard type diodes having comparable optical geometries. Values as high as 6% have been measured at 300°K when an antireflecting coat was applied to the four cleaved sides of a diode shaped to the form of a parallelepiped.<sup>2</sup> Without the coating, the external quantum efficiency was 3.7% for this particular diode. Values close to 3% for uncoated endfaces are quite commonly found. Comparable values for standard Zn-doped diodes of similar structure are approximately 1%.

The amphoteric behavior of Si is controlled essentially by the arsenic vapor pressure.<sup>3</sup> A GaAs crystal grown from a melt close to the stoichiometric composition becomes *n* type, as Si is preferentially incorporated on Ga sites and acts thus as a donor. Under reduced arsenic pressure, such as regrowth from a Ga-rich melt, however, Si is predominantly incorporated as an acceptor on As sites. It is therefore possible in a solution-regrowth experiment, by careful selection of temperature range and cooling cycle, to grow initially a highly compensated *n*-type region, which is followed finally by a highly compensated *p*-type region as the regrowth temperature has decreased below a critical value. The width of this highly compensated region is controlled by starting temperature and cooling rate. In a typical regrowth run the conditions were chosen such that after the growth of an *n*-type layer of about 40  $\mu$  the conductivity changed to *p* character. Subsequently, the *p* side of the wafer was polished down to 50–60  $\mu$  and a 2- $\mu$ -deep *p*<sup>+</sup> layer formed by diffusing Zn in, at 650°C for 20 min. In Fig. 1(a) and (b), a typical view of one of the four cleaved faces is shown for a diode under forward bias. At 300°K the light-emitting region is about 40  $\mu$  in width. At 77°K the width of the active region decreased to 15  $\mu$ . Despite this decrease the external quantum efficiency was up by a factor of 6 compared to the room temperature values. Figure 2 gives the spectral distribution of such a light-emitting diode. At 300°K the energy peak is found to be at 1.334 eV, practically independent of diode current. At 77°K, however, the peak position shifted from 1.381 eV to 1.410 eV when the current density increased from 10 A/cm<sup>2</sup> to 330 A/cm<sup>2</sup>.

Control experiments, where we have tried to substitute Si acceptors by other *p* dopants such as Mn, Cd, and Zn, always resulted in narrow active

regions. Also, compensation by donor impurities gave no improved results. Generally for acceptor concentrations ranging from 10<sup>16</sup>–10<sup>17</sup> holes/cm<sup>3</sup> the external quantum efficiencies had been poor (few tenths of a percent).

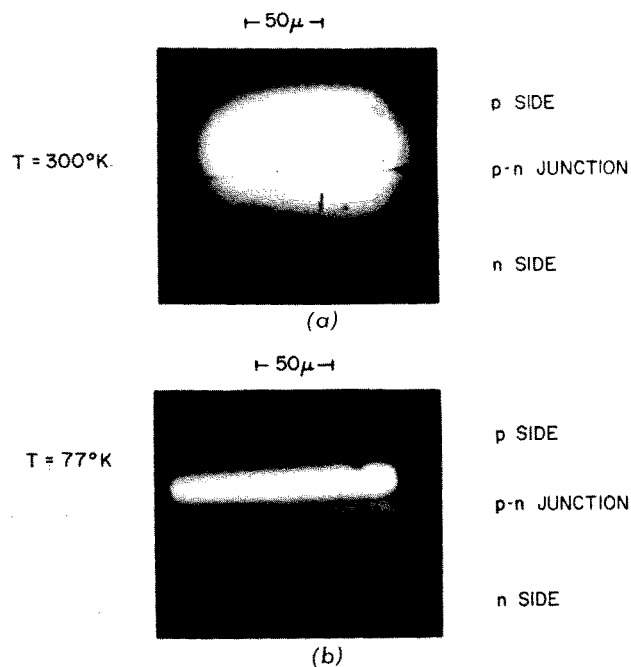


Fig. 1. View of a diode under forward bias.

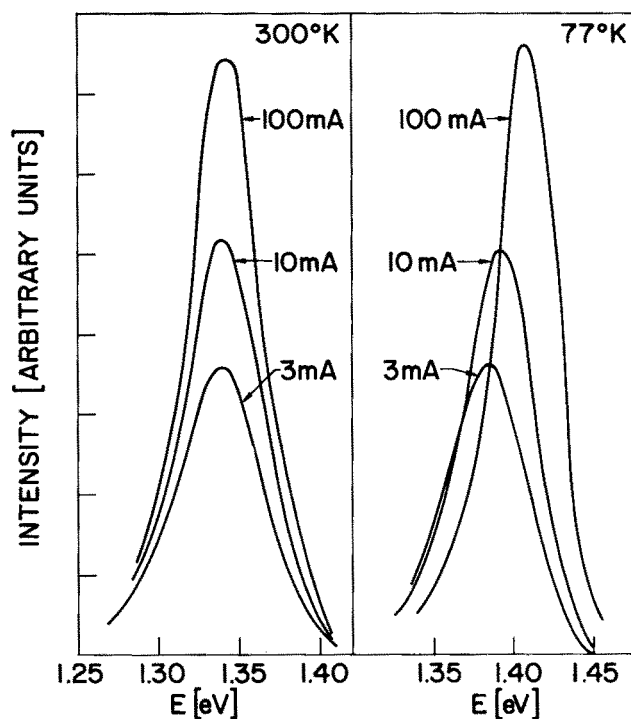


Fig. 2. Spectral distribution.

We believe that in these amphoterically-doped diodes the active region, at 300°K, is actually of the order of 50  $\mu$ . This conclusion is supported by results obtained from studies of the turn on time. Values up to 200 nsec have been found, depending on the diode current density. From a lifetime of 200 nsec and assuming a value for the electron mobility of 2500 cm<sup>2</sup>/V-sec, one derives a diffusion length of 35  $\mu$  which is the right order of magnitude.

The influence of the width of the  $p_0$  region upon the light-emitting properties was also studied. A set of 40 diodes was fabricated out of a wafer which had the  $p$  region lapped down in a wedge shape, thus varying from 20–50  $\mu$ . The external quantum efficiency decreased markedly with decreasing widths of the  $p$  region, as did the turn on time.

In summary, we have described the optical properties and the physical nature of efficient electroluminescence diodes, where the  $p$ - $n$  junction was completely solution-regrown and amphoterically-doped on both sides with Si in contrast to standard light-emitting diodes. The use of another amphoteric dopant of the group IV, Sn, was reported very recently by Winstel et al.<sup>5</sup> They found a very small temperature coefficient of the external quantum efficiency. In this case, a 10- $\mu$ -wide  $p$  layer was formed by alloying Zn-Sn into an  $n$  substrate. The reported efficiencies were about 1.4%.

We attribute the high external quantum efficiencies in our Si amphoterically-doped diodes essentially to reduced internal losses.<sup>4</sup> The reduction is due to a combination of two effects: (1) The energy of the emitted light is less than band gap; (2) the  $p$  side is highly compensated and gives rise to a wide light-emitting region, which is not highly absorbing.

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<sup>2</sup>There is only one instance where a value has been reported in the literature even somewhat higher than the ones discussed here. By shaping the diode to a semispherical geometry and coating the surface with an antireflecting film, W. N. Carr was able to obtain 7.3% external efficiency at room temperature. The  $p$  side of the junction was doped with Zn in that diode. W. N. Carr, *IEEE Trans. on Electron. Devices* **12**, 531 (1965).

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## PHOTON-MODULATED TUNNELING

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Infrared photoconductivity is obtained in a thin-film structure, Al-Al<sub>2</sub>O<sub>3</sub>-Te-Au, and the evidence suggests that it is due to photon-modulated tunneling.

Photoconductivity has been obtained in a metal-insulator-semiconductor structure, and the evidence suggests that it is due to photon-modulated tunneling. The spectral response is determined by the semiconductor. The present structure, which consists of a thin-film sandwich of Al-Al<sub>2</sub>O<sub>3</sub>-Te-Au, responds in the infrared.

Other photocurrent experiments on tunnel barrier structures have been concerned mainly with measurement of barrier heights in Al-Al<sub>2</sub>O<sub>3</sub>-Al

structures by internal photoelectric emission.<sup>1-3</sup> Visible or ultraviolet radiation is used, and generally it is presumed that hot electrons are generated in the aluminum electrodes and emitted over the 1.5- to 2-eV barriers. Other investigators,<sup>4</sup> however, interpret their (low-field) photoemission results as optical excitation of electrons from 1.8-eV traps in the oxide. The present experiment is concerned with the modulation of tunnel emission by photons, and it is believed that this effect is demonstrated for