Electroluminescence and Photoluminescence of GaAs at 77°K

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The electroluminescence from forward biased GaAs *p-n* junctions is compared with the photoluminescence of bulk homogeneously doped samples of GaAs. It is found that in the region of the absorption edge at ≈1.48 eV, the electroluminescence is similar to the *p*-type photoluminescence, while at lower photon energy the electroluminescence is similar to the *n*-type photoluminescence. The results show that centers responsible for the low-energy electroluminescence are present in the substrate and not introduced during the diffusion.

THE luminescence of forward biased GaAs *p-n* junctions has been studied by several workers.[1–4] In addition to the narrow line at about 1.48 eV near the absorption edge which gives rise to stimulated emission,[5–7] there are other emission lines at lower energy. Lines near 1 and 1.3 eV have been reported. While there is fairly good agreement among the various workers concerning the photon energy and shape of the line near the absorption edge, the reports of the relative strength of the low-energy emission lines and their photon energies differ considerably from one another.

The photoluminescence of bulk homogeneous samples of GaAs also has been investigated. In pure *n*-type material ($n<10^{17}$ cm^{-3}) at 4.2°K several sharp lines have been observed near the absorption edge.[8] At 77°K in this pure material, one sharp line near the energy gap is observed and has been attributed to recombination via an exciton state. In doped samples photoluminescence similar to both the low-energy emission in diodes[8,9] and the 1.48 eV line in diodes has been observed.[10] The correspondence between the 1.48 eV line in diodes and the *p*-type photoluminescence has been shown. The results suggested that the terminal state of the transition is an acceptor center.[10] The low-energy photoluminescence of crystals grown in oxygen has been studied.[11] The usual low-energy emission line is observed to be reduced in intensity by higher O_2 pressure and a line at 0.65 eV is introduced.

It is the purpose of this paper to examine in detail the correspondence between the photoluminescence on bulk-doped samples and the electroluminescence from diodes.

EXPERIMENTAL

Most of the GaAs crystals used in this study were pulled from quartz. Undoped crystals came out *n*-type, typically with a carrier concentration of 2×10^{17} cm^{-3} and a room temperature mobility in the 4000-cm^2/V sec range. The crystals were doped with Te for *n*-type, Zn for *p*-type during growth. Samples were lapped and then just prior to measurement etched so the surface appeared shiny. The diodes were made by diffusing Zn or Cd into *n*-type GaAs. All measurements were made at 77°K with the samples immersed in liquid N_2.

For photoluminescence, the samples were excited by a high-intensity mercury arc, filtered by a Cu_2SO_4 solution. The emission was observed from the same side of the crystal as the excitation so as to minimize the effect of self-absorption of the emission by the crystal. The measurements were performed with a grating or a prism monochromator. A PbS cell and a photomultiplier were used as detectors.

RESULTS AND DISCUSSION

Figure 1 shows the spectrum of a forward biased diode at low-current density (~10 A/cm^2) at 77°K, well below the threshold for stimulated emission. Stimulated emission occurs in the 1.48-eV line at higher current densities. In this diode, there are two low-energy emission lines: one at 1.02 eV and one at 1.28 eV. For different substrate crystals and diffusion runs there is considerable variability of the spectrum. For instance, the strength of the low-energy emission is about equal to that of the 1.48-eV line for some diffusion runs while for diodes made from other diffusion runs where the same *n*-type substrate was used but the time, temperature, and/or surface concentration of diffusant was varied, the low-energy emission has been observed to decrease by more than a factor of 50. In spite of this large variation of intensity of the low-energy emission with respect to the 1.48-eV line, the spectral shape of the low-energy emission varies little for different diffusion runs. No systematic difference was observed

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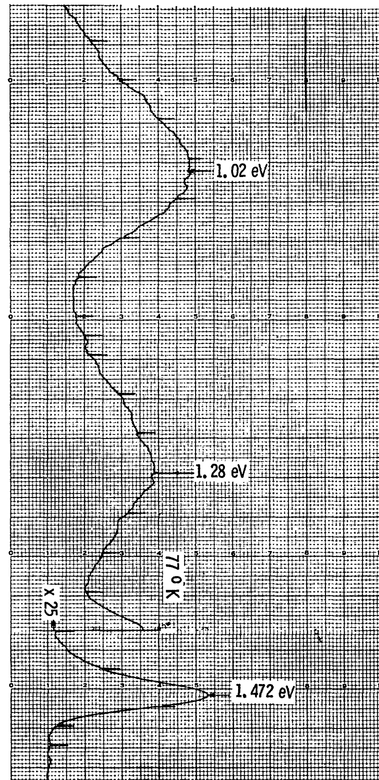

FIG. 1. Spectrum of GaAs diode at low-current density (10 A/cm^2). The line near the absorption edge is instrument slit width limited.

between Zn or Cd diffused diodes. However, the spectra of the low-energy emission do vary for diodes made from different n-type substrates. The variability of the intensity of the spectrum with diffusion parameters and the variation of emissions with n-type substrates are not understood. However, the variations in relative intensity and spectral shape are undoubtedly similar to the differences in spectra reported by different workers.[1–4]

Figure 2 shows typical photoluminescence spectra of n- and p-type samples at 77°K. The p-type emission is concentrated in a narrow line (about 0.02 eV wide) at 1.485 eV, which is just below the energy gap of pure material. There is a weak emission band at 1.25 eV. In contrast, the n-type emission is almost completely in the low-energy region. There is only a weak emission near the band edge at 1.515 eV.

a. Low-Energy Emission

A correspondence between the low-energy n-type photoluminescence and the low-energy diode emission can be seen. The diode of Fig. 1 was made from the n-type crystal, the photoluminescence of which is shown in Fig. 2. In the photoluminescence there is no peak at 1.28 eV, but both the diode emission and the photoluminescence have a peak very close to 1 eV.

The shape of the low-energy emission varies considerably from crystal to crystal. However, the shape of the low-energy diode emission is typically very similar to the low-energy photoluminescence of the n-type crystal from which it was made. A striking example of this is shown in Fig. 3 where the diode emission and the substrate crystal photoluminescence are plotted on the same graph. The diode emission and the photoluminescence have almost identical shape in the low-energy region.

The fact that the shape of the n-type low-energy photoluminescence correlates well with the low-energy diode emission and the fact that the low-energy emission is absent in the photoluminescence of p-type samples suggest that the diode emission is caused by recombination occurring in the n-type region. It also shows that the defect responsible for the recombination is not introduced during the diffusion. The variability of the spectrum suggests that more than one kind of center is involved. Feinlieb *et al.*[12] have also concluded from high-pressure measurements on the low-energy emission in diodes that more than one center may be involved in the transition. They found different pressure coefficients for the photon energy of the peaks in different diodes. Larsen[13] has found that copper can give rise to emission at 1 eV.

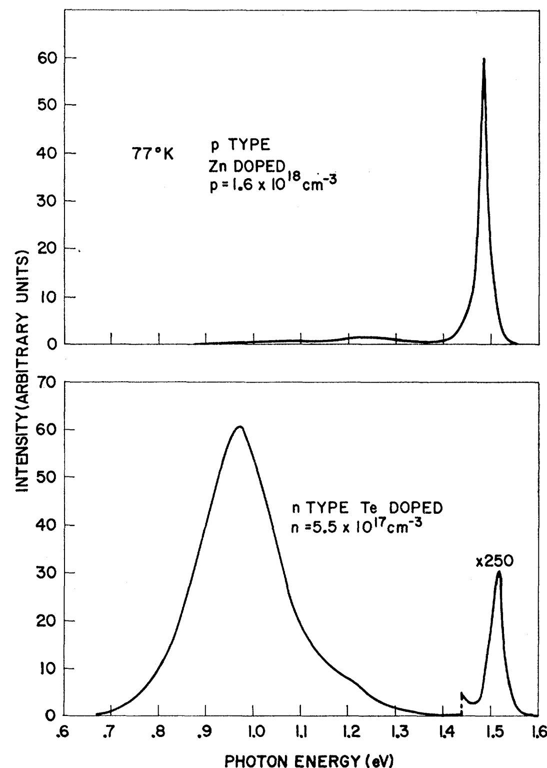

FIG. 2. Photoluminescence of n- and p-type GaAs. Spectra uncorrected for the wavelength dependence of the transmission of the spectrometer.

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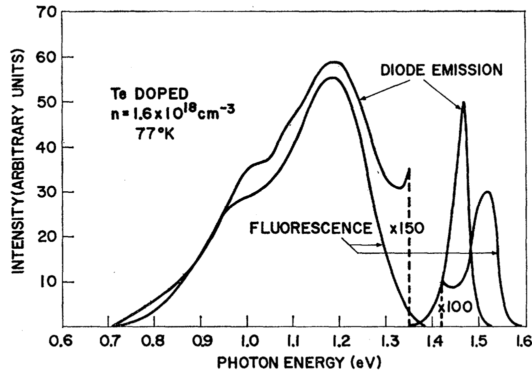

FIG. 3. Photoluminescence and electroluminescence (diode emission) from the same n-type substrate. Spectra uncorrected for the wavelength dependence of the transmission of the spectrometer.

There are some additional facts which lend strength to the argument that the low-energy recombination occurs in the n region. First, some high-purity n-type crystals pulled from AlN[14] show little or none of this low-energy photoluminescence. Diodes made on one of these crystals show none of the low-energy emission. Second, photoluminescence measurements made on n-type samples diffused with Zn show low-energy emission from the region of the samples where Zn has not penetrated and the sample is still n-type. While from the Zn diffused p-type region there is no low-energy emission.

b. Emission Near the Absorption Edge

Figure 4 shows the emission in the region of the absorption edge for two n-type (Te-doped) and two p-type (Zn-doped) samples. Both types of emission broaden considerably with increasing concentration. The p-type emission is one to two orders of magnitude stronger than the n-type emission.

In Fig. 5, the energy of the peak of the edge emission versus carrier concentration at 77°K is plotted. The energy gap in pure material is indicated by E_g for reference. There are three curves: (1) The peak of the n-type photoluminescence, (2) the peak of the p-type photoluminescence, (3) the peak of the emission from the diodes. The abscissa for this last curve is the n-type substrate-electron concentration before diffusion. For diodes, it has been observed that the peak of the emission increases in energy with increasing injection current.[15–18] This shift saturates at ≈ 1000 A/cm^2. It is the high-current value of the peak energy that is plotted in Fig. 5. The shift is only an apparent one. Actually, the low-energy side of the line saturates, and as one increases the current the high-energy side of the line grows. This behavior is consistent with injection into states tailing from the band edge. No such shift is observed in the photoluminescence results despite the fact that the level of excitation corresponds very roughly to about 1 A/cm^2 current in the diodes. In this current range the diode emission is shifting rapidly. A possible explanation for this is that optically excited minority carriers are generated at energies well above the bottom of the band. It may be that the recombination time is smaller than the thermalization time into the tailing states. In the diodes, on the other hand, carriers can be injected directly into the tail.

The peak of the n-type photoluminescence at low-carrier concentrations is very close to the energy gap of pure material as can be seen in Fig. 5. Similar spectra are observed in Si and Se doped samples. At the higher concentrations there is a small shift to higher energy. If the initial states of the transitions are conduction band states, this shift is probably caused by the Burstein-Moss shift, i.e., a filling of the conduction band by electrons. Similar spectra have been observed by Hill.[19] He has also observed a similar shift of the absorption edge in n-type samples to higher energies, which he has interpreted quantitatively in terms of a Burstein-Moss shift.

The Zn photoluminescence starts out at about 1.485 eV and shifts to lower energy with increasing concentration by about 0.04 eV. Hall effect and resistivity measurements on p-type GaAs show no evidence of de-ionization for concentrations greater than[20] 2×10^{18} cm^{-3} so that the impurity level is merged with the valence band over almost the whole concentration range. The shift indicates a decrease of E_g at higher

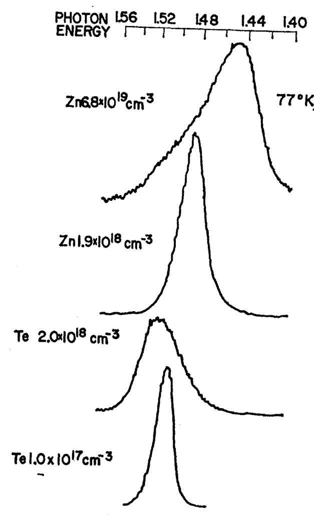

FIG. 4. Photoluminescence near the absorption edge at 77°K.

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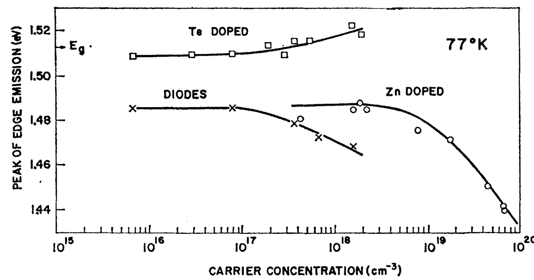

FIG. 5. Photon energy of the peak of the luminescence versus carrier concentration.

concentrations. There is no evidence of a Burstein-Moss shift to higher energy in the p-type emission. It is expected that this shift would be much smaller than in n-type samples since the effective mass is much smaller and the shift to higher energy is masked by the energy gap decrease with increasing concentration. The fact that the Zn photoluminescence in the most lightly doped samples is well below the band gap in pure material suggests that the transition in the p-type samples has as its terminal state the energy level of the acceptor center. This level is merged with the valence band at high concentration. Cd-doped samples give spectra similar to the Zn-doped samples. However, only two samples were measured both with carrier concentration between 1×10^{18} cm^{-3} and 2×10^{18} cm^{-3}. The photoluminescence near the absorption edge of Cd-doped GaAs has been more extensively studied by Hill.[19] He finds a line at about 1.484 eV at concentrations down to 6×10^{16} cm^{-3}.

The diode curve is similar to the Zn curve and then shifts to lower energy. The fact that the maximum energy of the Zn photoluminescence equals the maximum energy of the diode curve and the fact that, at high concentrations, they both shift to lower energy, suggest that the emissions are caused by the same transition and that the diode emission comes predominantly from the p-side of the junction. For a given n-type carrier concentration one expects to inject into the p region and because of the large gradient of concentration at the junction, one expects to have recombination radiation corresponding to some larger carrier concentration of Zn. Thus, the diode curve should be displaced from the Zn curve as they are in Fig. 5.

It appears that the transition is between the conduction band or a donor level and an acceptor center which, at high concentration, is merged with the valence band. For electron concentrations of 8×10^{16} cm^{-3} and higher, Hall effect and resistivity measurements show no evidence of de-ionization,[20] so that the donor level is probably merged with the conduction band.

With regard to the regions from which the emissions are coming, there is a direct method of obtaining information about this at least for the edge emission, namely visual observation of the junction[21] with a microscope and an image converter or infrared film. The results of this experiment appear to be complex, however. In some junctions, a rather broad emitting region 5 to 15 μ thick clearly on the p side of the junction is observed. In others the emission appears to be coming from a narrow region, two microns thick or less, in the vicinity of the junction.[21,22] The difference between these junctions is not clearly established. If the region of recombination is very thin ($<1\mu$), then descriptions like p side or n side lose significance. In this case, the photoluminescence results indicate that the recombination is occurring in a region where acceptors are present at a high concentration.

These photoluminescence measurements do not necessarily mean that none of the diode edge emission is coming from the n side of the junction. The n-type photoluminescence is well into the absorption edge. If the diode emission coming from the n-side of the junction has the same spectral distribution as the photoluminescence, it will be strongly self-absorbed. This will mean that its apparent peak will be shifted to lower energy toward the observed diode emission. However, the high external quantum efficiencies[3,23] observed in GaAs junctions indicate that, with respect to the laser line, the n-side contribution is small. Moreover, the shift of the absorption edge to higher energy with increasing concentration would decrease the self-absorption effect at high concentrations. Thus, the photon energy of diode emission coming from the n side might be expected to increase at higher concentration; however, the observed emission decreases.

ACKNOWLEDGMENTS

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