(3.14) of Ref. 5, we calculate a peak photocurrent of 25 mA/cm^2 from the thoriated tungsten surface when a ruby laser beam of power density 20 MW/cm^2 is incident on the surface at an angle of 52° between the direction of polarization and the surface normal. This current density should have been easily detectable with this apparatus and should have occurred at a time when it would not be masked by thermionic emission. There was no trace of electron emission from thoriated tungsten with the right time dependence for two photon effect. If such emission was present, it must have been considerably smaller.

In the calculations of temperature rise given in Figs. 3 and 4, reflectivity of the surface has been neglected; it was assumed that all energy in the laser beam was absorbed. The inclusion of reflection of energy from the surfaces would tend to increase the differences between the experimental and theoretical curves in Figs. 3 and 4. The results indicate that a considerable portion of the energy was absorbed, even though the surfaces appeared initially shiny. As the surface begins to heat early in the high power density pulse, the absorption may increase rapidly. Other results[3] on the depth of holes vaporized in metallic surfaces also indicate that a large fraction of the energy in the laser pulse is absorbed.

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Injection Luminescence in GaAs by Direct Hole-Electron Recombination

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Luminescence from GaAs *p-n* junctions was measured under conditions where spectral distortion due to self-absorption was $\leq 15\%$. Spectra were observed through a 2–3-μ-thick Zn-diffused *p*-type layer ($C_0 \simeq 5\times10^{19}$ cm^{-3}) and a thin Au contact. Junctions in a float-zone-refined crystal, $n=2\times10^{16}$ cm^{-3}, showed a dominant emission band with peak energies of 1.423 and 1.508 eV when measured in ambients of 298 and 77°K, respectively. This band is attributed to direct hole-electron recombination resulting from hole diffusion into the *n*-type region of these *p-n* junctions. Supportive evidence includes good correspondence with the calculated emission peak based on detailed balancing arguments and optical absorption data, independence of peak energy on junction voltages at low current densities, and agreement with photoluminescent data for *n*-type GaAs. The recombination process responsible for this band is significant for diodes with $n=2.3\times10^{17}$ cm^{-3} at room temperature, but not at 77°K, nor for diodes with $n=2\times10^{18}$ cm^{-3} at either temperature.

SPONTANEOUS injection luminescence of forward biased GaAs *p-n* junctions has been measured with special emphasis on the reduction of spectral distortion. Principal sources of distortion are self-absorption and internal reflection within the GaAs. A new emission band has been observed from junctions made by Zn diffusion into lightly doped *n*-type samples where $n=0.2$ to 2×10^{16} cm^{-3}. The above emission band at 298 and 77°K matches the one calculated from Sturge's absorption data,[1] the principle of detailed balance, and the assumption of a negligible contribution by phonon-assisted transitions. This agreement supports Sturge's energy assignment of the direct energy gap of GaAs at these temperatures. We attribute this band to direct hole-electron recombination on the *n*-type side of the junction under conditions where the conduction band minimum and valence band maximum are essentially unperturbed by low concentrations of impurities. In the context of this report, direct recombination includes radiative recombination via free exciton annihilation and direct band-to-band transitions, i.e., those responsible for absorption at the edge.

The diode structure shown in Fig. 1 was used to reduce spectral distortion of luminescence originating in the vicinity of the junction. The 120-μ-thick *p*-type layer on the back side was made by Zn diffusion for 5 h at 750°C from a ZnO-GaAs powder source in a sealed ampule.[2] This serves as an absorber for that radiation not absorbed in the *n*-type region and acts as the equivalent of an antireflective coating. The active junction 2–3 μ below the top mesa surface was made subsequently by a similar diffusion for 2 h at 650°C. Surface concentrations of the shallow and deep diffused layers are estimated to be 5×10^{19} and 2×10^{20} cm^{-3}, respectively. The shallow *p* layer was contacted by reaction

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* On leave of absence from the Instituto Technologico de Aeronautica, Brazil.

[1] M. D. Sturge, Phys. Rev. **127**, 768 (1962).

[2] L. A. D'Asaro (private communication).

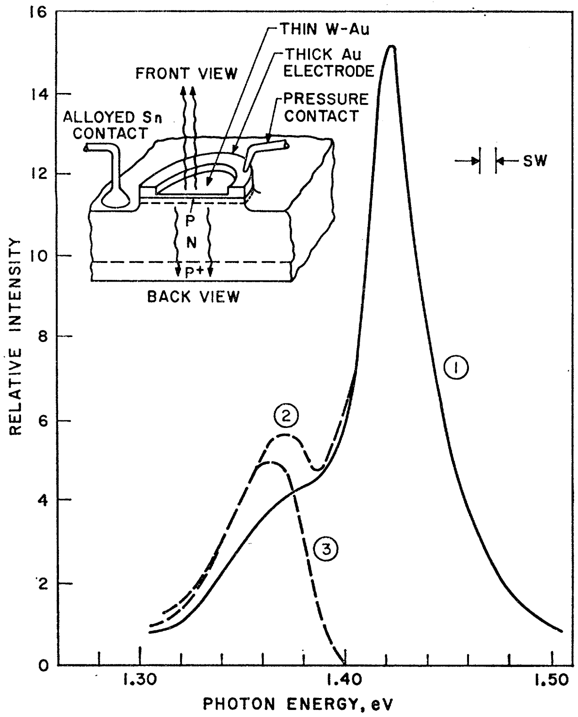

FIG. 1. Spontaneous emission at 300°K from a Zn diffused p^+n diode. No. 1 spectrum observed through the W-Au window of the structure shown in the insert; No. 2, similar conditions but without the backside p^+ absorbing layer; No. 3 spectrum observed through the n-type layer after removing the absorber.

with WF_6 in Ar at 350°C[3] and electroplated with Au to adjust the sheet resistance to 1 $\Omega/\square$ or less. This contact is used as a window. The over-all optical density of the thin p-type layer and the metal films is estimated to vary by less than 15% over the spectral range of interest based on the absorption data for p-type GaAs[4,5] and the optical constants of the metals. Approximately 50% of the area of the W-Au contact was overplated with a thick annular Au ring and external contact made to it. The voltage drop to the center of the thin W-Au area is conservatively estimated to be less than 2 mV for current densities under 20 A cm^{-2}. It is important that this IR drop be low as many of the previously reported emission bands shift with applied voltage. Alloyed tin was used as the n-type contact. As a final step, the front surface was covered with an opaque Apiezon W wax except for the window.

Figure 1 illustrates the emission spectra with varying degrees of distortion from a lightly doped np^+ Zn diffused diode. Spectrum No. 1 was obtained through the metal window of the configuration shown in the insert with its front face masked. We believe this spectrum is essentially an undistorted representation of that originating in the vicinity of the junction. The low-energy shoulder may be an artifact. Its intensity relative to the major peak does vary from one diode to another but it can be enhanced by cracks or pinholes in the wax mask. Spectrum No. 2 was obtained under similar conditions except that the p^+ absorber was removed and the back n-type side polished. After normalization at their peak intensities the two spectra are identical for photon energies >1.403 eV. The extraneous low-energy peak of No. 2 at 1.37 eV is due to the enhanced intensity of nonabsorbed radiation reflected from the back side of the 300-μ-thick n-type layer. Spectrum No. 3, obtained from the backside without the absorber, was normalized at 1.35 eV. The extraneous peak energies of Nos. 2 and 3 depend on the reflectivities of the diode surfaces, thicknesses of the n- and p-type layers, their absorption coefficients and the emission spectrum originating at the junction. Spectra have been generally reported which represented the radiation emitted through the back surface or in a direction parallel to the plane of the junction. We have been unable to obtain undistorted spectra of spontaneous recombination radiation in the latter case. Calculated corrections for self-absorption are difficult except for heavily doped diodes because the absorption coefficients can vary from ~ 10 to 10^4 cm^{-1} over the spectral range of interest.

Figures 2 and 3 show the emission through the window of a diode in ambients of 298 and 77°K, respectively. The active junction was made as previously

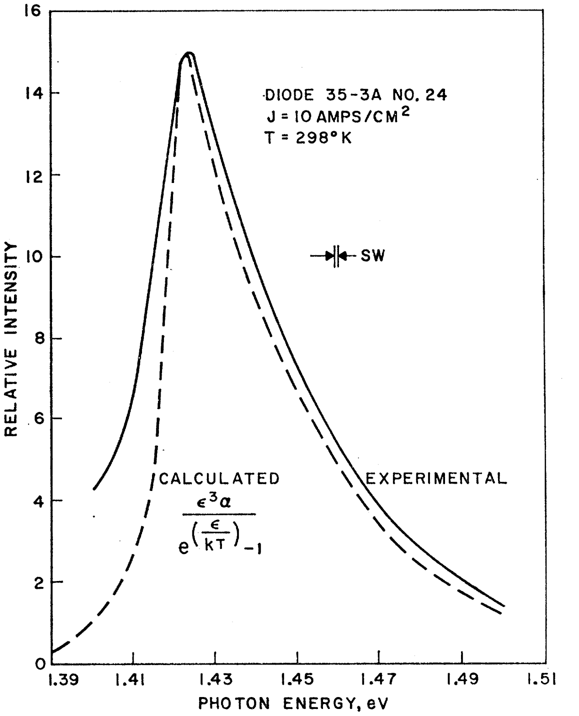

FIG. 2. Comparison of the calculated and observed emission bands at 298°K. The diode structure is shown in Fig. 1.

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[4] I. Kudman and T. Seidel, J. Appl. Phys. **33**, 771 (1962).

[5] D. E. Hill, Phys. Rev. **133**, A867 (1964).

described by Zn diffusion into S-doped GaAs in which $n=2.0\times10^{16}$ cm^{-3}. At room temperature the capacitance varies as voltage^{-2} indicating a step junction with a net donor concentration on the lightly doped side within 10% of the initial electron concentration. Peak energies and widths at half intensity are 1.423 and 1.508 eV, 0.038 and 0.010 eV, respectively, at 298 and 77°K. These are independent of current density below $\simeq$20 A cm^{-2}. Above this current density heating is noticeable at room temperature by a shift in peak intensity to lower energies. At 77°K there are secondary bands with peak intensities at 1.485 and 1.36 eV (not shown in Fig. 3). The dashed spectral curves in these figures were calculated from Sturge's absorption data extrapolated from 294 to 298°K and interpolated between 90 and 21 to 77°K, using the principle of detailed balance and the assumption that phonon-assisted transitions were unimportant. The index of refraction required for this calculation was assumed to be 3.6 at both temperatures, the maximum variation is less than 10%.[6] For these assumptions, the relative intensity of the calculated curves is proportional to the product of the absorption coefficient α at a photon energy ϵ and the blackbody distribution function, $\epsilon^3(\exp \epsilon/kT-1)^{-1}$. The main emission lines shown in Figs. 2 and 3 are attributed to direct hole-electron recombination on the n side of the junction; diffusion is probably the injection mechanism. Supportive evidence for this recombination mechanism is the self-consistency of these spectra with the absorption data, photoluminescence spectra of lightly doped n-type GaAs, and the independence of the photon energy at peak intensitise on applied voltage or current densities. These will be discussed separately.

The peak intensities of the calculated spectra were normalized to those observed. Energies at the peak intensities of the observed spectra are 0.001 eV less than the calculated peaks, a discrepancy which may be due to a reasonable uncertainty in the absorption data, an actual junction temperature 2° above its ambient or a hole diffusion length $\simeq 1\ \mu$. Widths of the two emission bands agree within 30% at 298°K and 10% at 77°K. Sturge used for his absorption measurements semi-insulating GaAs which had an estimated total impurity concentration of 10^{16}–10^{17} cm^{-3}. No significant change in α is expected as n is increased to 2×10^{16} cm^{-3} in the critical range where $\alpha \geq 2500$ cm^{-1}, i.e., $\epsilon \geq 1.41$ eV. This is supported by the absorption data of Hill[5] and Spitzer and Whelan.[7] The observed peak intensities are at energies less than Sturge's values of the direct gap, 1.432 and 1.514 eV at 298 and 77°K, respectively. These peak intensities correspond to absorption coefficients of 7800 and 8300 cm^{-1} which occur on the low-energy side of the absorption maxima as expected.

At 77°K the 1.508 eV peak agrees with the photoluminescent peak energy reported by Nathan and Burns[8] for lightly doped n-type GaAs although their half width was 50% of ours. This can be qualitatively explained by the enhanced transport of "hot" carriers generated by their mercury arc prior to their radiative recombination and self-absorption. Our observed peaks are also in good agreement with Hill's[5] photoluminescent data at 300 and 77°K for n-type GaAs.

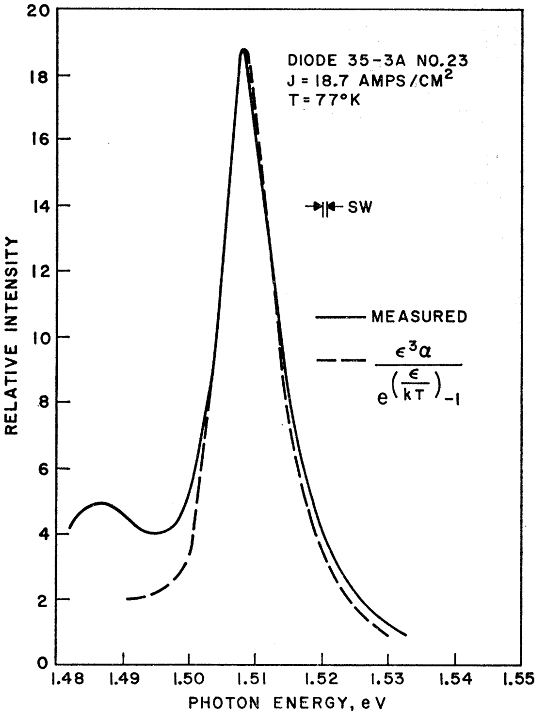

FIG. 3. Comparison of the calculated and observed emission bands at 77°K. The diode structure is shown in Fig. 1.

The current density independence in peak energies of the major band shown in Figs. 2 and 3 also argues for recombination on the n-type side of the junction. Band filling effects would be minor on that side where the impurity concentrations are low. Diffusion is probably the hole injection mechanism because the integrated intensity of the 1.508-eV band in Fig. 3 varies as $\exp qv/1.1kT$. This is within our experimental uncertainty of the expected dependence for diffusion, $\exp qv/kT$. Wilson[9] reported a similar variation for an emission band at 1.505 eV which may be the same as the 1.508-eV band but modified by self-absorption.

The intensity ratio of the 1.508 to 1.485-eV bands in Fig. 3 increases with current density over the measured range 1–20 A cm^{-2}. This is as expected if the 1.484-eV band is associated with the recombination of electrons in the conduction band[10] or in a shallow band tail[11] with

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[9] D. K. Wilson, J. Appl. Phys. Letters **3**, 127 (1963).

[10] W. F. J. Hare, M. Gershenzon, and J. M. Whelan, Solid State Device Research Conference, Durham, New Hampshire, 1962 (unpublished).

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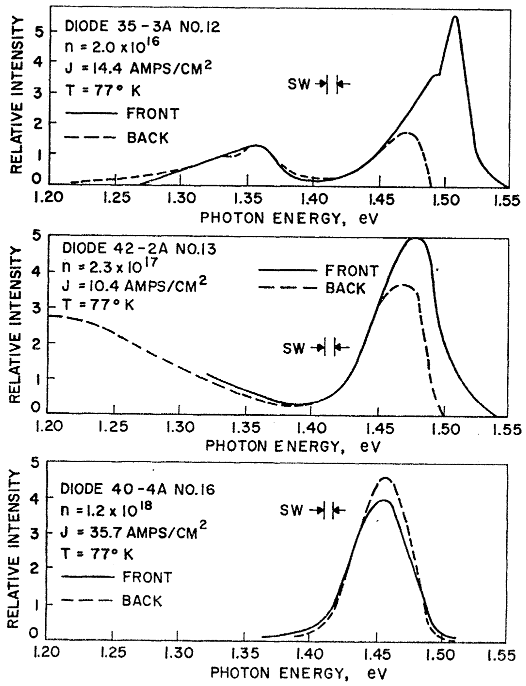

FIG. 4. Spectra at 300°K from Zn diffused diodes with varying electron concentrations on the n-type side. Solid spectra were observed through the window of the structure shown in Fig. 1 but without the p^+ absorber. The dashed spectra were observed through the n-type side.

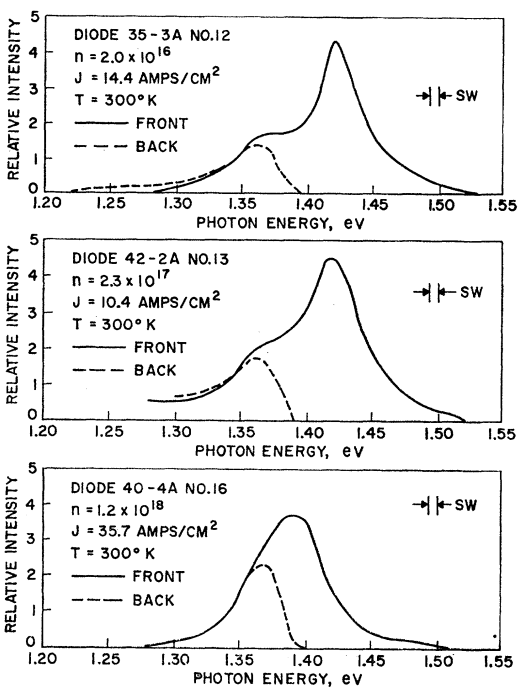

FIG. 5. Spectra at 77°K obtained under the same conditions as those in Fig. 4.

holes at Zn acceptors on the p-type side of the junction. This is in accord with photoluminescent data for p-type GaAs.[5,12] Variation in the above ratio could be either a variation in the hole to electron minority carrier injection currents or exhaustion of holes on Zn acceptors. We suggest the former is more likely. The p-type side consists of a transition region where the net acceptor concentration varies from $\sim 10^{20}$ cm^{-3} at the surface to $\sim 10^{16}$ cm^{-3} at the junction over a distance $\sim 2\,\mu$. The average conductivity varies from that characteristic of degeneracy to impurity banding and possibly hole freeze-out on isolated Zn acceptors.[13] The conductivity typical of both impurity banding and carrier freeze-out is temperature and electric field dependent. Neglecting changes in lifetimes, the ratio of hole diffusion current limited by carrier freeze-out to electron diffusion current at low fields should vary as exp E_A/kT, where E_A is the acceptor ionization energy. Wilson reported a variation of exp $0.025/kT$ in the intensity ratio of bands with peak intensities at 1.505 and 1.48 eV.[9] We estimate the Zn acceptor level to be $\simeq$0.026 eV above the valence band by subtracting the 1.485 band from the gap, 1.514 eV, and taking the energy of an exciton bound to the Zn acceptor as the sum of the ionization energy and the binding energy of the free exciton, 0.003 eV.[1] The ratio of hole-to-electron injection currents should increase with current density because of the associated voltage drop across the p-type region. A field of 10 to 100 V cm^{-1} would increase the conductivity of the p-type layer whose zero-field conductivity were typical of impurity banding or carrier freeze-out. Voltage drops $\gtrsim$0.020 V would be sufficient for layers $2\,\mu$ thick to affect the ratio.

Diodes made by Zn diffusion into more heavily doped GaAs with $n = 2\times 10^{17}$ and 1×10^{18} cm^{-3} emit a significant fraction of their radiation at photon energies in excess of the gap at 300°K. This fraction decreases with increasing donor concentration and is negligible at 77°K for the highest electron concentration. Figures 4 and 5 illustrate these changes. The solid curves were observed through the W-Au window and a 2–3-μ-thick p^+ layer, but without an absorber on the back side. The dashed curves were spectra viewed through the n-type side. For the more heavily doped diodes energies at maximum intensities of the major peaks vary with current density. This is consistent with the expected changes in ratios of hole to electron diffusion and tunneling currents and band filling effects. These will be considered in a subsequent paper.[11]

Estimates of the internal quantum efficiency of the lightest doped diode were 1–10% at 300°K. Its external efficiency was the smallest of the three diodes in Fig. 4 because of strong self-absorption.

ACKNOWLEDGMENTS

We wish to thank R. G. Sobers and F. Ermanis for providing the GaAs crystals and Hall data on them.

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