atoms are removed in taking away one lattice plane to form the dislocation, we expect a negative dislocation charge as in Ge. However a positive core charge is found[8,9,20] experimentally, at least in low-angle grain boundaries grown from the melt. The explanation we suggest is that excess Sb atoms are grown in substitutionally near the core during crystallization, and more work on dislocations produced by plastic deformation would therefore be of interest. At the grain boundary during growth there will be dipolar electric fields alternating in sign as the crystal grows. There is therefore no net attraction of In or Sb atoms due to their charge, but the field gradient would preferentially attract Sb atoms since these will be somewhat larger, "softer," more polarizable.

In silicon a positive core charge has also been reported,[21] which cannot, of course, be explained by the mechanism suggested for InSb. It is presumably due to other causes than those considered in the present paper. However, it should be noted that in our theory, the removal of some volume, or what is the same thing, a local excess atom density, will lead to the repulsion of levels out of the valence band and, hence, a positive core charge. Now the diamond structure is of course very open, and germanium for instance shrinks on melting. It is therefore not impossible, though unlikely, that the atom density in the disordered region in the core of the dislocation is somewhat higher than in the bulk, accounting for a positive core charge in silicon.

It is a pleasure to acknowledge stimulating conversatons with Dr. R. K. Mueller, and the warm hospitality of Bell Telephone Laboratories during the summer of 1964 when this work was started.

[20] H. C. Gatos, M. C. Finn, and M. C. Lavine, J. Appl. Phys. **32**, 1174 (1961).

[21] See, for example, Y. Maturkura, Jap. J. Appl. Phys. **2**, 91 (1963).

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High-Energy Emission in GaAs Electroluminescent Diodes

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A study of high-energy photon emission ($h\nu - eV \gg kT$) from various GaAs diodes is reported and the results analyzed. We find that this emission is produced by most diffused diodes except those doped with Sn and Ge. It is not observed in solution-grown diodes, no matter what the doping. It is always accompanied by a large amount of excess (nonradiative) current and can be explained in terms of the Auger recombination of carriers at defects with subsequent diffusion of the excited electrons to the p side of the junction.

INTRODUCTION

During the past few years considerable work has been done on the electroluminescence of forward-biased GaAs diodes at wavelengths near the absorption edge. This work has been directed toward experimentally characterizing the electro-luminescence and identifying the various recombination mechanisms involved. Pankove[1] reported that the emission line near the edge, which gives rise to the laser action at high current densities, shifts to higher photon energy with increasing current. He attributed his results to tunneling with photon emission. Shortly afterward a correspondence between this edge electroluminescence and the photoluminescence of homogeneously doped p-type samples was reported, indicating that an acceptor is involved in this transition.[2]

Subsequently it was found that the shift reported by Pankove resulted from a tendency of the low-energy side of the line to saturate and the high-energy side of the line to increase super-linearly with current.[3,4] It was also found by Nelson *et al.*[3] that the photon energy of the peak of the line $h\nu_1$ satisfied

$$h\nu_1 = eV + \delta E, \qquad (1)$$

over a range from 1.3 to 1.5 eV, where V is the applied voltage and δE is a small correction (a few meV) which depends on temperature. It was suggested[3,4] that the shift was caused by a filling up of an exponential tail on the conduction band density of states which comes about as a result of the high density of impurities and/or mobile carriers. Archer *et al.*[5] found that Eq. (1) holds for applied voltages as small as 1.1 V. In the voltage range from 1.1 to 1.3 V these workers presented evidence for tunneling into the forbidden gap with photon

[1] J. I. Pankove, Phys. Rev. Letters **9**, 283 (1962).

[2] M. I. Nathan and G. Burns, Appl. Phys. Letters **1**, 89 (1963).

[3] D. F. Nelson, M. Gershenzon, A. Ashkin, L. A. D'Asaro, and J. C. Sarace, Appl. Phys. Letters **2**, 182 (1963).

[4] M. I. Nathan and G. Burns, in *Quantum Electronics 3, Proceedings of the Third International Congress of Quantum Electronics*, edited by P. Grivet and N. Bloembergen (Columbia University Press, New York, 1964).

[5] R. J. Archer, R. C. Leite, A. Yariv, S. P. S. Porto, and J. M. Whelan, Phys. Rev. Letters **10**, 483 (1963).

emission, the mechanism originally proposed by Pankove.[1] More recently[6,7] it has been suggested that tunnelling generally predominates at low current densities while band-tailing effects are important at high currents.

In addition to the peak shift line (line I) many diodes exhibit an emission line (line II) which does not satisfy Eq. (1) and occurs at energies substantially greater than eV.[6,8]

Detailed results for diodes which exhibit line II are given in this paper and several possible mechanisms for its production are considered. We show that it is not due to a refrigeration effect[9] or a surface effect and that the process responsible must involve the recombination of more than a single electron-hole pair. An explanation involving Auger recombination at a defect center is presented and discussed.

DIODE CONSTRUCTION

Three types of diodes were studied: (1) diffused, (2) alloyed, (3) solution-grown. Most of the diodes were made with n-type substrates diffused with zinc at 850°C for 2–3 h in an evacuated quartz tube containing 0.3 mg/cm^3 of Zn_3As_2.[10] They were usually in the form of laser structures through other configurations were also used. No dependence of spectral properties on geometry was observed. The substrate crystals were grown by the Czochralski technique or were boat grown by S. Blum and J. Woodall of this laboratory. The electron concentrations determined from Hall effect and resistivity measurements were between 7×10^{15} cm^{-3} and 6×10^{18} cm^{-3}. The alloyed diodes were made by rapidly alloying Te-doped Sn dots into Zn-doped substrates. The solution-grown diodes were made by regrowing Zn-doped GaAs on Te-doped substrates or vice versa.[11]

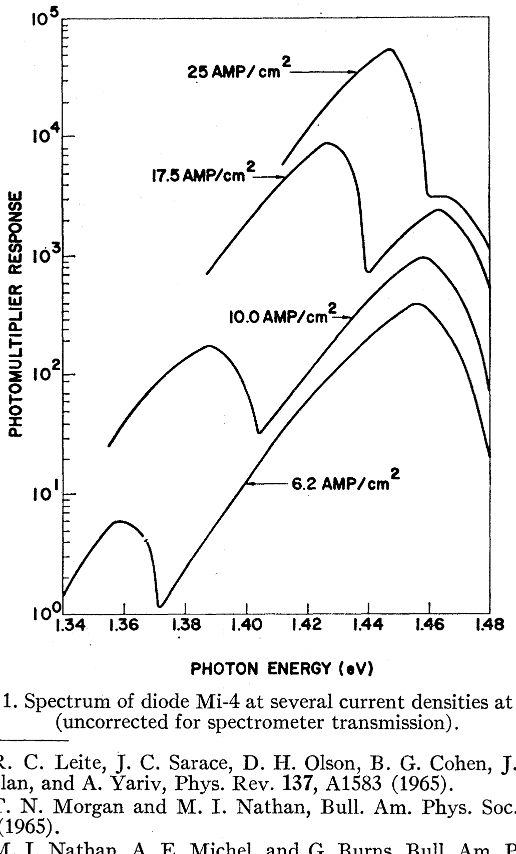


FIG. 1. Spectrum of diode Mi-4 at several current densities at 2°K (uncorrected for spectrometer transmission).

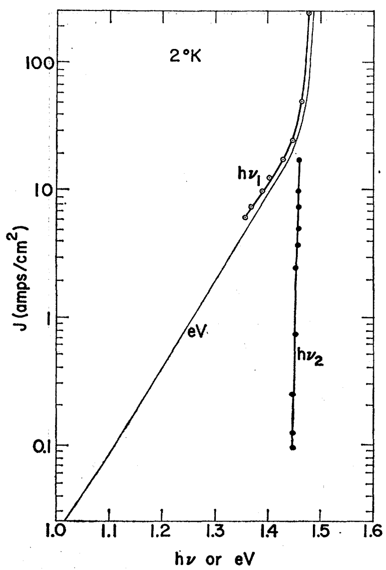


FIG. 2. Current density versus voltage and photon energies $h\nu_1$ or $h\nu_2$ for diode Mi-4. $J\propto\exp(15.6V)$.

RESULTS

In addition to line I which obeys Eq. (1), the electroluminescence of the alloy diodes and most of the diffused diodes (except those doped with Sn or Ge) exhibit a second line (line II) at low current densities which is always associated with a large amount of excess (nonradiative) current. The photon energy of line II is almost independent of current and is close to the value for line I at high current densities. The most significant feature of line II is that its energy is considerably greater than the applied voltage.

We shall now give the results of detailed measurements for one diode (Mi-4) which exhibits line II over a wide range of current density. The diode was made from a selenium doped crystal with an electron concentration of 2.1×10^{18} cm^{-3}. Other diodes made from similarly doped crystals give almost identical results. Diodes made from crystals with other kinds of impurities (except for Sn) yield results which are qualitatively

[6] R. C. Leite, J. C. Sarace, D. H. Olson, B. G. Cohen, J. M. Whelan, and A. Yariv, Phys. Rev. **137**, A1583 (1965).
[7] T. N. Morgan and M. I. Nathan, Bull. Am. Phys. Soc. **10**, 389 (1965).
[8] M. I. Nathan, A. E. Michel, and G. Burns, Bull. Am. Phys. Soc. **9**, 269 (1964).
[9] G. C. Dousmanis, C. W. Muller, H. Nelson, and K. G. Petzinger, Phys. Rev. **133**, A316 (1964).
[10] J. C. Marinace, J. Electrochem. Soc. **110**, 1153 (1963).
[11] H. Nelson, RCA Rev. **24**, 603 (1963).

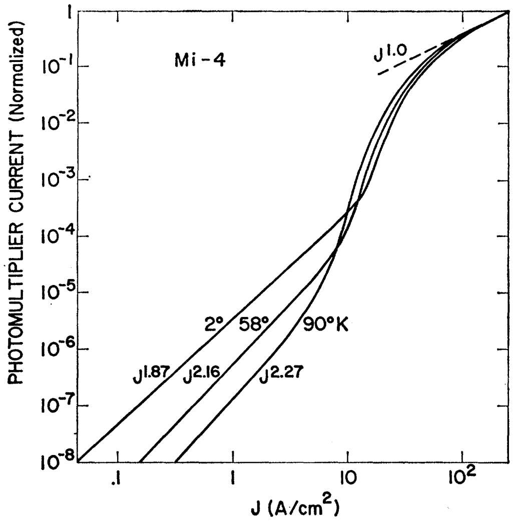


FIG. 3. Light intensity versus current density. Curves have been normalized at high current. The data were taken with an S-1 response photomultiplier.

similar. Sn-doped diodes exhibit neither line II nor the excess current, and we show in the final section that this offers a key to the explanation.

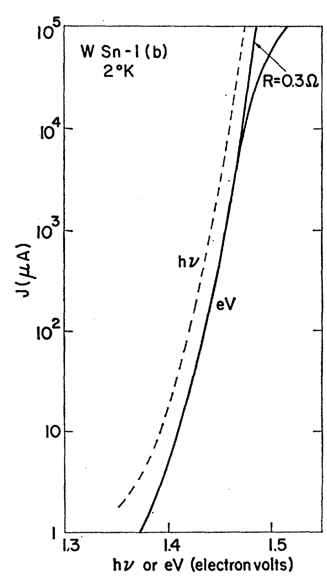
Figure 1 shows the spectrum of diode Mi-4 at 2°K at several current densities for which both emission lines are visible. The line at lower energy (line I) shifts with current and obeys Eq. (1) with $\delta E=-0.012$ eV at 2°K. This can be seen in Fig. 2 which is a plot of current density versus voltage and peak photon energy. At 77°K $\delta E=+0.015$ eV. For a given current density $h\nu_1$ is the same at 77 and 2°K, though eV at 77°K is 0.027 eV less than at 2°K. The photon energy of line II versus current is also shown in Fig. 2. It can be seen that at low current densities at 2°K $h\nu_2$ is as much as 0.34 eV greater than the applied voltage. Figure 3 shows the results of measurement of the total light intensity L (no spectrometer) as a function of current density J at 2, 58 and 90°K. The curves are normalized at high current where the quantum efficiency has been found in a separate experiment to be essentially temperature independent between 2°K and 90°K. At low currents line II is predominant, and at 2°K L is proportional to $J^{1.87}$. There is a rapid rise in the intensity starting where line I becomes dominant, near 10 A/cm^2, and L approaches J^6 at medium currents. At high currents L is proportional to J. Similar behavior is observed at higher temperature as can be seen in the figure except that the intensity in the low current region is about an order of magnitude less than it is at 2°K. The external quantum efficiency, measured in an integrating-sphere-type apparatus[12] at 77°K was found to be 6% in the high current region and was nearly independent of temperature.

In order to distinguish between bulk and surface processes, the importance of recombination at the surface of the semiconductor was investigated as follows. Several diodes were measured, then etched electrolytically for 10 sec in KOH and measured again. Both the current density and light output at a given voltage were found to have decreased by as much as 50%. However, the ratio of the integrated intensities in the two lines at a given voltage was found to be the same before and after etching. Thus, unless both lines were caused by surface effects, the mechanism responsible for line II cannot involve the surface.

Several properties of the diodes were measured in an attempt to establish a correlation with the appearance of line II. In particular, long-wavelength emission (from 1μ to 2.5 μ) was examined and found to have no correlation. Line II was observed in diodes which did, as well as in those which did not exhibit long wavelength emission. The rise and decay times of line II were found to be less than 10^{-8} sec, the response time of the measuring system, and hence could not be measured.

The method of fabrication of the diodes influenced the presence of line II in a complex manner. Three types of diodes were studied: diffused, alloyed, and solution-grown. In the diffused diodes the presence of line II depended on the nature of the substrate donor impurity. The line was emitted from Se- and Te-doped diodes, but not from Sn- and Ge-doped diodes. In Sn-doped diffused diodes line II was completely absent and the current was proportional to the intensity of line I. Figures 4 and 5 show the results for a typical Sn-doped diode. Diodes made from some Si-doped crystals exhibited the line while those from others did not. Several diodes made by alloying 1% Te-Sn dots into a Zn-doped substrate exhibited the line. An example is shown in Fig. 6. In contrast, solution-grown diodes did not show the high-energy line no matter what the doping was.

FIG. 4. Current versus voltage and photon energy for a Sn-doped diode of area, $A=1.6\times10^{-4}$ cm^2. The effect of series resistance is indicated.



[12] G. Cheroff, F. Stern, and S. Triebwasser, Appl. Phys. Letters 2, 173 (1963).

For example, some solution-grown diodes were made by regrowing n material from a Te-doped solution. These diodes did not show line II but Zn-diffused diodes made on the solution-regrown material did. Some of these observations are discussed in the next section where we consider processes which can cause emission of light of high energy.

DISCUSSION

It might appear that line II is caused by the recombination of carriers injected across the junction from the tail of the thermal (Boltzmann) distribution similar to the refrigeration effect reported by Dousmanis *et al.*[9] That this is not the case is clear from the following discussion. On the basis of such an explanation the intensity of line II would be expected to increase with increasing temperature as does the density of carriers in the tail. However, it can be seen in Fig. 3 that the intensity of line II *decreases* with increasing temperature. The argument can be made stronger from thermodynamic considerations. From the first and second laws of thermodynamics[9] it can be shown for a recombination process involving one electron-hole pair that the difference between the photon energy of the peak of the line and the applied voltage is

$$h\nu_2 - eV < kT \ln(1+1/X) \approx kT \ln(1/X), \quad (2)$$

where X = number of photons per electromagnetic mode. X can easily be calculated in terms of the current density and the quantum efficiency. If we assume unit quantum efficiency in Fig. 3 at high current density we find the right-hand side of Eq. (2) equal to 0.0038 eV at 2°K for the lowest current density measured in Fig. 2. The experimental value from Fig. 2 at 0.1 A/cm^2 is 0.33 eV. Clearly, line II cannot be caused by the recombination of a single electron-hole pair in thermal equilibrium. Somehow more than one electron-hole pair must be involved. Similar effects have been observed in II-VI compounds.[13]

To construct a consistent model we use the fact that the curves in Figs. 2 to 6 show a correlation between the high energy emission and the excess current. Thus for diode Mi-4, Figs. 1 and 3 show that $J \propto L_1^{1/6}$ and $L_2 \propto J^2$ (approximately) while for the alloy diode $J \propto L_1^{1/2}$ but again $L_2 \propto J^2$. On the other hand, for a Sn-doped diode, W Sn-1, line II is not observed and, as can be seen in Fig. 5, $J \propto L$. These results can be understood in terms of tunneling processes together with Auger recombination at localized centers.[14] In the tunneling model the peak shift emission (line I) is produced by photon-assisted tunneling across the junction and is associated with a current flow $J_1 \propto L_1$ (though not necessarily with unit quantum efficiency). This agrees with results for diode W Sn-1 with $J = J_1$. When localized recombination centers are present in the junction, an additional "excess" current J_2 can flow which is not proportional to L_1 and which exceeds J_1 at low currents. It is shown in Ref. 14 that a single type of center produces a current $J_2 \propto L_1^{1/2}$ in agreement with data from the alloy diode, while the cooperation of more than one type of center causes a current given by $J_2 \propto L_1^{1/n}$ with $n > 2$. An example of this last case is provided by diode Mi-4 with $n \approx 6$. The Auger recombination occurs when two carriers interact with a trapped carrier in such a way that the recombination energy is transferred to one of them exciting it into the conduction or valence band. This process occurs at a rate $\propto L_2$ which is lower than the principal recombination rate and varies approximately as its square, $L_2 \propto J^2$. If the carrier is excited to an energy above the barrier height, it can diffuse across the junction and recombine with a majority carrier near the junction edge. The emission will be characteristic of the material in that part of the device and of the states through which the radiative recombination occurs. Changes in bias voltage have little effect on the emission spectrum except

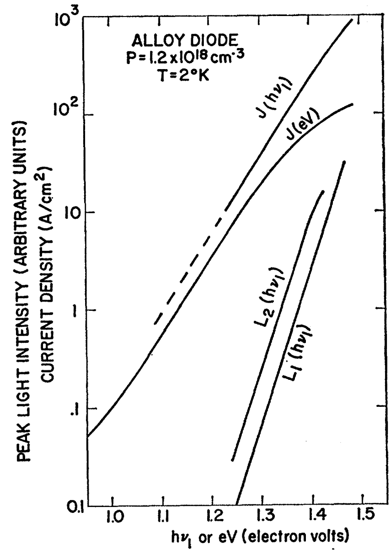


FIG. 6. Current density and peak light intensities versus voltage and photon energy $h\nu_1$ for an alloy diode. The slopes are $J \propto \exp(18.4 h\nu_1)$ and $L \propto J^{2.0}$. The intensities have been corrected for spectrometer transmission.

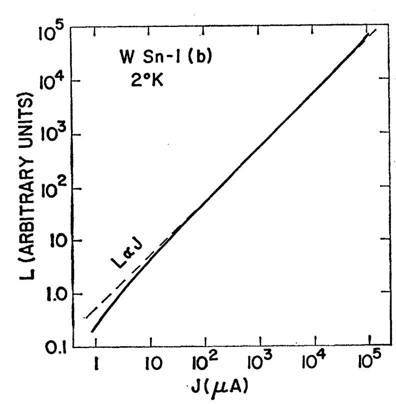


FIG. 5. Total light intensity versus current for a Sn-doped diode. A correction has been made for the (S1) response of the phototube.

[13] M. Aven and D. A. Cusano, J. Appl. Phys. 35, 606 (1964).

[14] T. N. Morgan, Phys. Rev. (to be published).

through motion of the recombination maximum relative to the junction edge. Similarly, changes of the diffusion rate (and of the Fermi function) with temperature can produce spectral changes if the maximum recombination rate shifts to more or less heavily compensated materials, though these shifts produce only small changes in the intensity.

We can use the temperature dependence of the light intensity (as shown in Fig. 3) to interpret the excitation process for the high energy emission. The peak shift light (line I) accounts for most of the emission above a current of about 10 A/cm^2 while below 2 A/cm^2 almost all of the light is produced in the high energy line (line II) as can be seen in Fig. 1. The strong decrease in the light intensity at low current with increasing temperature suggests that the radiative recombination occurs through localized states from which the carriers can be released thermally. The nonradiative loss of the thermally excited carriers (probably by their being swept away in the junction field) accounts for the observed temperature dependence. To interpret these results quantitatively we must know which processes account for the nonradiative loss, since different models lead to different values of the activation energy.

Consideration of several models has shown that the activation energy is small—between 0 and ~40 meV—and that the emission occurs through recombination centers lying close to a band edge, probably shallow donors or acceptors. The peak shift emission (near $J=18$ A/cm^2 in the figure) varies approximately as $L_1 \propto J^6$ and indicates that the current flow occurs through two or more types of centers.[14] In another diode showing a different L_1-J dependence the flow might pass through a different set of intermediate defect states and produce Auger excitation of minority carriers into either or both bands. In the absence of active defect states we should find $L_1 \propto J$ and line II absent as seen in Figs. 4 and 5 for a Sn-doped diode.

At 2°K the emission peak of diode Mi-4 appears near 1.46 eV for $J \approx 2.5$ A/cm^2 (as can be seen in Fig. 2) but falls by a few hundredths of an eV at lower currents and rises by about the same amount at the higher temperatures. These energies are close to the peak energies observed from photo-luminescence in p-type material and from electroluminescence observed from the p sides of similar diodes,[15] suggesting that electrons are injected into the p side of the diode. Further evidence for this assignment of the Auger emission to the p-side is found in the emission spectra from this same diode under reverse bias.[16] Two emission peaks are seen in this case, one with a peak at 1.46 eV which is the same as for the Auger emission and one with a peak near 1.50 eV—presumably from the n side of the junction. This higher energy line was not observed in the Auger (low current) emission for any of the diodes studied.

The role played by Sn in suppressing the high-energy emission (or by the Se etc. in producing it) is not understood. The importance of the donor impurities in controlling both the emission of line II and the flow of excess current strongly suggests that the presence or absence of defect states is the determining factor. The effects produced by Sn (and some other group-IV impurities) may result from their amphoteric properties. These impurities act as donors on Ga sites, but can also act as acceptors on As sites. Thus they may tend to deactivate recombination centers associated with As vacancies or other defects and to reduce or eliminate the current through these centers. Although the exact nature of this mechanism is not known, the presence of deep traps in many of these diodes (including Mi-4) has been established from measurements of capacitance.

In summary, we have found that high energy emission ($h\nu$-$eV \gg kT$) and excess (nonradiative) current occur together in most diodes but are absent in Sn and Ge-doped diodes. We have shown also that these effects cannot be explained in terms of surface or refrigeration effects but can be understood in terms of nonradiative current flow through recombination centers with an associated Auger excitation of electrons to energies above the junction barrier.

ACKNOWLEDGMENTS

It is a pleasure to thank J. A. Bradley for technical assistance, and J. C. Marinace, H. Rupprecht, and R. F. Rutz for the diodes used in this study.

[15] A. E. Michel, E. J. Walker, and M. I. Nathan, IBM J. Res. Develop. **7**, 70 (1963); M. I. Nathan, G. Burns, S. E. Blum, and J. C. Marinace, Phys. Rev. **132**, 1482 (1963).

[16] A. E. Michel, M. I. Nathan, and J. C. Marinace, J. Appl. Phys. **35**, 3543 (1964).