similar to $^5D_0 \rightarrow {}^7F_2$, that is, whereas the intensity above 110°K is due principally to vibronic transitions, both zero-phonon and vibronic structure are observed below 110°K (the calculated probability for magnetic-dipole transitions is very low). Such lines can arise due to changes in the symmetry of the local crystalline fields at the impurity sites and the resultant modifications of the selection rules for fluorescence transitions. Although electric-dipole transitions are forbidden in cubic crystalline fields O_h due to inversion symmetry, they are allowed in lower symmetry fields such as tetragonal C_{4v}. The energy-level decomposition of the various J states and selection rules for allowed transitions in C_{4v} symmetry can easily be derived. Lines such as those appearing below 110°K are predicted for this symmetry. Thus the present spectrum illustrates a situation in which transition probabilities and line intensities are more sensitive indicators of the phase transition and changes in the crystalline field than are energy-level splittings.

ACKNOWLEDGMENTS

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Effect of Deep Levels on the Optical and Electrical Properties of Copper-Doped GaAs *p-n* Junctions

T. N. Morgan, M. Pilkuhn,* and H. Rupprecht*
IBM-Watson Research Center, Yorktown Heights, New York

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Three types of GaAs *p-n* junctions containing diffused copper impurities were fabricated and studied. Careful investigation of their electrical characteristics and optical emission spectra were carried out over a wide range of current between 4 and 300°K. Broad emission peaks near 1.34, 1.29, and 1.06 eV (at low temperatures) are identified with transitions involving the interstitial copper donor and the first and second substitutional copper acceptor levels having binding energies of $E_c - E_{\text{donor}} = 0.07$ eV and $E_{\text{acceptor}} - E_v = 0.18$ and 0.41 eV, respectively. A similar peak near 1.00 eV is attributed to an unidentified donor level lying 0.5 eV below the conduction band. External quantum efficiencies were generally low, indicating the presence of an appreciable amount of nonradiative recombination. The existence of impurity conduction in the copper donor band of graded diodes containing large concentrations of copper ($>6\times10^{18}$ cm^{-3}) is deduced from the disappearance at 77°K of all emission peaks except that at 1.34 eV. These diodes exhibited negative resistance ($dV/dI \lesssim 0$) above a breakdown voltage of 10 to 20 V. Alloy diodes in similar material showed negative resistance of the tunneling type ($dI/dV \lesssim 0$) above 0.3 V at room temperature. Some of the centers frequently seen in laser-type diodes by their emission near 1.0 eV and by their effects on capacitance are shown not to be due to copper.

1. INTRODUCTION

THE electrical behavior of copper impurities in gallium arsenide has been investigated by several workers.[1–6] A very detailed study was recently carried out by Hall and Racette.[7] It is believed that substitutional copper on a gallium site gives rise to two acceptor levels, a first ionization level near 0.14 eV[1,5,6] and a second ionization level near 0.45 eV above the valence band.[2,3,7,8]

In the electroluminescence of GaAs laser diodes, two low-energy emission peaks near 1.28 and 1.00 eV have been observed[9] at 77°K. Larsen[10] suggested that the 1.00-eV peak is due to the presence of copper in these diodes. In diodes which had a background doping of copper, he found a strong emission peak at 0.95 eV at room temperature which was absent in diodes with a similar heat treatment but no copper doping.

In this paper it will be demonstrated that copper impurities can give rise to additional emission lines, including lines in the neighborhood of 1.3 eV at 77°K. Besides junctions containing copper as a background

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* The work of these authors was supported as part of Project Defender under the joint sponsorship of the Advanced Research Projects Agency, the U. S. Office of Naval Research, and the U. S. Department of Defense.

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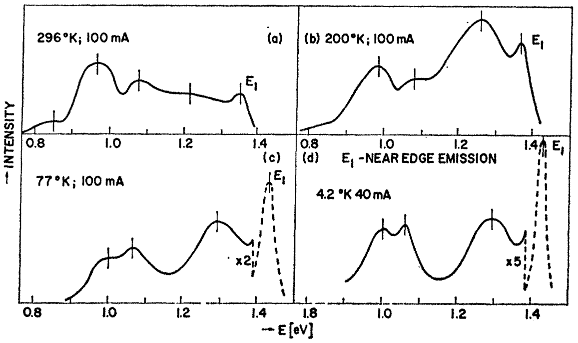

FIG. 1. Emission spectra of a type I diode at four different temperatures (measured with a cooled PbS detector). (Diode area: 2.4×10^{-4} cm^2.)

dopant, diodes which contained copper as the only added acceptor were also studied.

The material is organized as follows: In Secs. 2 through 7 we describe the experimental techniques and results. The theories of line shapes and of distribution of the copper ions are presented in Secs. 8 and 9 and are used to interpret the emission spectra of the diodes in Secs. 10 through 14. In conclusion, the capacitance and conductance measurements are analyzed in Secs. 15 through 17.

2. DIODE FABRICATION

Three different types of *p-n* junctions involving copper impurities were fabricated. In the first (diode type I) Zn was diffused at 850°C for $2\frac{1}{2}$ h into an *n*-type substrate with 2×10^{18} donors cm^{-3}.[11] Subsequently, copper was electroplated and diffused into these wafers at 1000°C for 90 sec. This resulted in a sufficiently low copper background doping to avoid converting the *n* region.

Diodes containing copper as the only acceptor impurity (diode type II) were fabricated by diffusing copper into *n*-type material (10^{18} cm^{-3} Te donors) for a very short time (less than 1 min). This resulted in a junction depth of 9 μ.

A third type of diode (type III) was made by converting an *n*-type substrate material containing 2×10^{18} cm^{-3} Te donors into *p* GaAs by copper diffusion at 1060°C for 5 min. Junctions were made by alloying tin into this material.

Typical dimensions of all these diodes were $130\times80\times80$ μ.

3. INFLUENCE OF COPPER BACKGROUND DOPING ON LUMINESCENCE

The light emission from diodes of type I was investigated at various temperatures and currents, and typical emission spectra are shown in Fig. 1. Besides band-edge emission, several broad emission lines can be observed at lower energy. The intensity of the edge emission decreases relative to that of the low-energy lines with increasing temperature. At 300°K, the low-energy emission can easily exceed the band-edge emission in intensity. Three impurity emission lines are prominent at low temperature: a line at 1.28 eV and two at about 1.0 eV (77°K) with peaks at 1.07 and 0.99 eV. In addition, at the higher temperatures another line near 0.84 eV is evident which is not observed at low temperatures, probably because of overlap with the 0.99-eV line. No further light emission could be detected down to 0.4 eV.

All impurity lines in diodes of this type have a much larger half-width than does the edge emission at low temperature. (See Table I.) At 4.2°K, for instance, the edge emission has a linewidth at half-maximum of 24 meV, whereas the 1.29-eV line has a width of 146 meV, and the 1.06- and 1.00-eV lines 75 meV. At 77°K, the band-edge linewidth increases to 60 meV. All lines were skewed toward low energy except the 1.06-eV line which showed a tail extending toward higher energies. [This is visible in Fig. 2(b).]

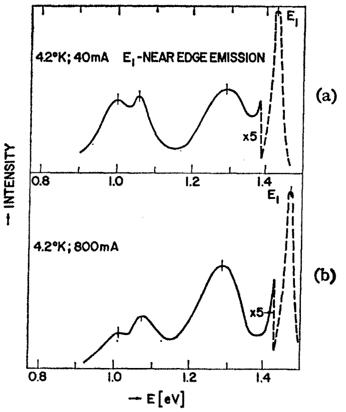

FIG. 2. Influence of current on the emission spectra of a type I diode at helium temperature. (Diode area: 2.4×10^{-4} cm^2.)

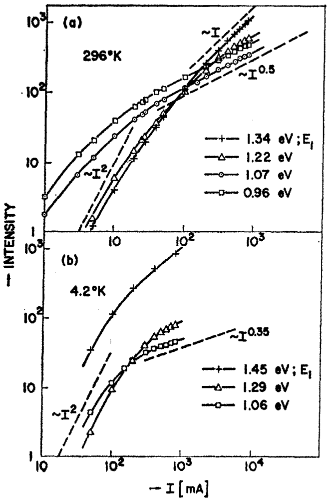

FIG. 3. Intensity versus current dependence for several emission lines of type I diodes. The intensities are the peak intensities of the lines. (Diode area: 2.4×10^{-4} cm^2.)

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[11] M. H. Pilkuhn and H. Rupprecht, Trans. AIME 230, 282 (1964).

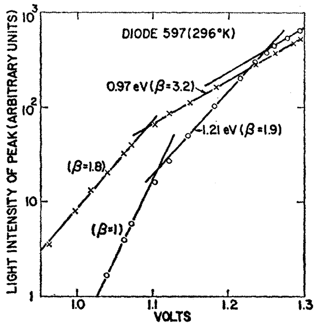

FIG. 4. Intensity versus voltage dependence for two of the lines of Fig. 3(a). A correction for *IR* drop has been included above 1.2 V.

The dependence of the spectral distribution on current density is illustrated in Fig. 2 for helium temperature. It can be seen that the edge emission shifts to higher energy when the current is increased. This is the peak shift commonly observed in GaAs diodes. The impurity lines, however, show little or no shift of their peaks (less than 10 meV), though their widths and skewness may change with voltage.

Another point of interest in Fig. 2 is the dependence of the relative line intensities on current. With increasing current, emission in lines with higher energy is favored. This was found to be a general rule for all lines and all temperatures. In particular, this is evident in the case of the two lines near one eV (4.2 and 77°K) where the high-energy line becomes more and more dominant at higher currents. In the low-current range, the two peaks are nearly equal in intensity and might be mistaken for one broad peak.

The dependence of the peak intensities of various emission lines on current I and voltage V was studied for different temperatures (Figs. 3 and 4). At all temperatures, the edge emission increased in the low-current range as I^2, and in the high-current range linearly with I. At 300°K, the 0.96- and 1.22-eV lines vary as $I^{1.5-2.0}$ at low currents and as $I^{1/2}$ at high currents. Writing the voltage dependence as $\exp(eV/\beta kT)$, we find: for the 0.96-eV line $\beta\approx 2$ for $V<1.09$ V, $\beta\approx 3.2$ above 1.09 V. For the 1.22-eV line $\beta\approx 1$ below 1.11 V, $\beta\approx 2$ from 1.11 to 1.25 V, and $\beta\approx 3.2$ above 1.25 V as shown in Fig. 4. At helium temperature, the same current dependence is observed with the exception that the impurity lines vary as $I^{0.35}$ rather than $I^{1/2}$ in the high-current range.

The external quantum efficiency η of these diodes was measured at 77°K with an integrating chamber using Si photodiodes as detectors.[12] The average value of η at current densities of 5000 A/cm^2 was found to be 2×10^{-3}. This is about one-tenth of the external quantum efficiency of the spontaneous emission of average laser diodes at that temperature. Even if we consider that one-fourth of the emitted photons will not be counted because the Si detectors are sensitive only down to 1.09 eV, the low value of η suggests that there is appreciable radiationless recombination. This makes it understandable that laser action in copper-doped diodes could not be observed.

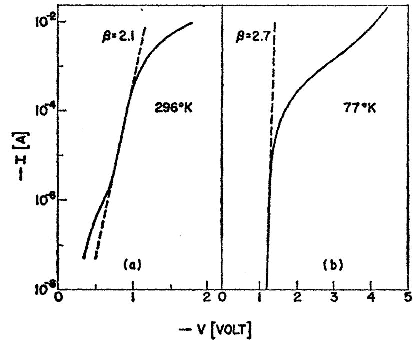

FIG. 5. Current-voltage characteristic of type II diodes at liquid-nitrogen and room temperatures. The 77°K curve shows only the pre-breakdown region. (Diode area: 1.9×10^{-4} cm^2.)

4. BEHAVIOR OF JUNCTIONS CONTAINING COPPER AS THE ONLY ACCEPTOR IMPURITY

The electrical behavior of diodes of type II which contained a 9-μ-thick copper-doped p region with no other acceptors added was investigated. The current-voltage characteristic at room temperature is shown in Fig. 5(a) in a semilogarithmic plot. Above 0.7 V, the current varies as $\exp(qV/\beta kT)$ where β is 2.1. Below 0.7 V, there is a transition region with a larger β value, and at lower voltage the same dependence as for high currents is again approached. At nitrogen temperature the thin copper-doped region of the diode becomes rather highly resistive. At high voltages a negative resistance behavior can be observed, as shown in Fig. 6. The "breakdown" generally occurs when 10 to 20 V are applied across the diode. After breakdown the voltage approaches 2–5 V. The current-voltage characteristic before breakdown has been plotted in Fig. 5(b).

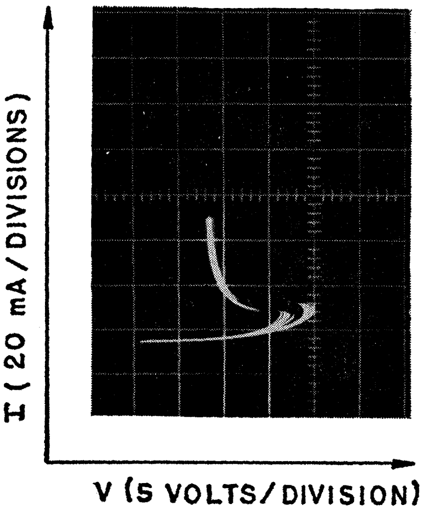

FIG. 6. Current-voltage characteristic of a type II diode at 77°K showing breakdown at high voltage.

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[12] G. Cheroff, C. Lanza, and S. Triebwasser, Rev. Sci. Instr. 34, 1138 (1963).

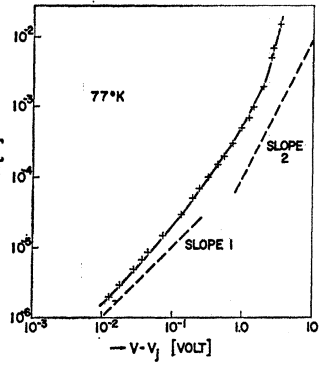

FIG. 7. Prebreakdown current-voltage characteristic of a type II diode at 77°K. The junction voltage V_j has been subtracted from the total applied voltage V. $V_j(I)$ was determined previously by plotting log I versus V (compare Fig. 5(b) dotted line). (Diode area: 2.5×10^{-3} cm^2.)

At very low currents an exponential dependence of current on voltage with a β value larger than two is valid [$\beta=2.7$ in the case of Fig. 5(b)]. At higher currents the applied voltage exceeds the junction voltage V_j obtained by extrapolation of the low-current line, until the curve bends back at breakdown. A plot of current as a function of excess voltage $V-V_j$ (Fig. 7) gives a linear dependence of current on $V-V_j$ at low currents (corresponding in the figure to a series resistance of about 6500 Ω). As the current is increased, the resistance decreases by more than a factor of 100 before breakdown ($dV/dI=0$) is reached. According to a theory by Ashley,[13] injection into an insulating region with traps present should lead to a linear current-voltage relationship at low currents and a quadratic dependence at high currents which is not observed in Fig. 7. Better agreement with this theory was found by K. Weiser[14] for GaAs diodes which contained a highly resistive manganese-doped region.

The room-temperature electroluminescence of type II diodes is depicted in Fig. 8(a). It shows no bandgap emission but only broad impurity lines with peak energies of 1.29, 1.22, 1.07, and 0.97 eV. The last three energies and the line shapes closely coincide with those observed in diodes of type I (Fig. 1). The 1.29-eV line, which was not seen in diodes of type I at this temperature, becomes more intense at lower temperature [Figs. 8(b)–8(d)] and at 77°K its peak energy, 1.35 eV at low current, coincides with an emission line often observed in photoluminescence of p-type GaAs.[15] At 300°K, this line was nearly symmetrical with a width at half-maximum of 130 meV. At 77°K, above breakdown it became slightly skewed toward low energies with a half-width near 100 meV. Occasionally, a small amount of edge emission could be observed at 77°K [Fig. 8(c)] when the diode was nearly at breakdown, or if a reverse bias was applied. Above breakdown, the intensity increased strongly and occurred only near 1.35 eV [Fig. 8(d)]. The external quantum efficiency of this radiation was 2×10^{-4}, i.e., about 1% of that of laser-type diodes. An observation of the diode under a microscope and an infrared image converter showed that the light originated at the p-n junction below breakdown and in the entire p region above breakdown. The reverse bias emission at 77°K seemed to occur in definite spots at the junction and produced two nearly symmetrical peaks—one at 1.33 eV with a half-width of 110 meV and a band edge peak at 1.46 eV with a half-width of 48 meV.

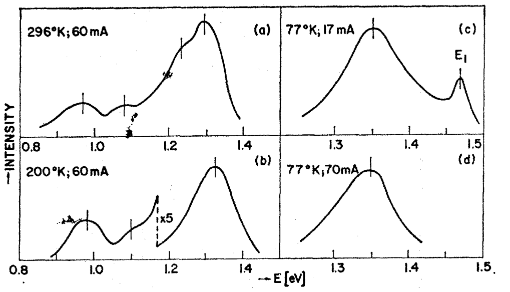

FIG. 8. Emission spectra of type II diodes at three different temperatures. The curve in Fig. 8(c) was measured very close to breakdown, the curve in Fig. 8(d) after breakdown. (Diode area: 7.5×10^{-5} cm^2.)

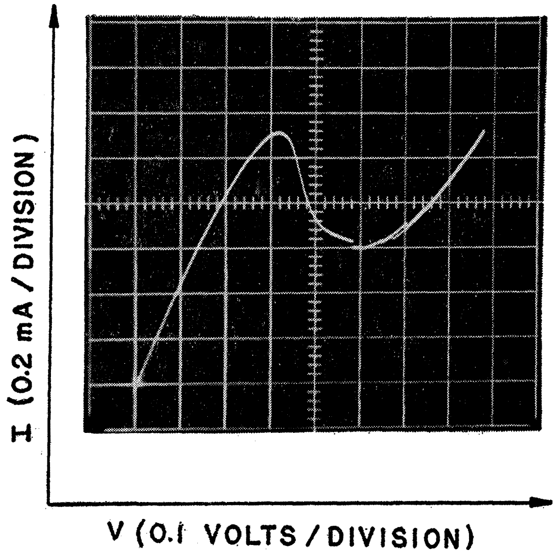

FIG. 9. Current-voltage characteristic of a type III diode at room temperature showing negative resistance (tunnel diode characteristic).

5. ALLOYED JUNCTIONS IN COPPER-DOPED p-TYPE GaAs

Diodes of type III frequently showed a negative resistance with a peak-to-valley current ratio of up to two. A typical current-voltage characteristic of these negative resistance diodes is shown in Fig. 9. A secondary kink which appears about 0.2 V above the dominant one is assumed to be associated with the second

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[13] K. L. Ashley and A. G. Milnes, J. Appl. Phys. **35**, 369 (1964).

[14] K. Weiser, R. S. Levitt, and W. P. Dumke, Bull. Am. Phys. Soc. **8**, 201 (1963); K. Weiser and R. S. Levitt, J. Appl. Phys. **35**, 2431 (1964).

[15] W. J. Turner (to be published).

ionization level of the copper centers. Those diodes which did not show negative resistance were presumed to have lost active copper through precipitation or the gettering action of the tin. Hall measurements made on the diffused material before alloying indicated a carrier concentration of between 10^{16} and 2×10^{17} holes/cm^3 at 300°K with an activation energy of 0.15–0.17 eV.[16] Of three samples analyzed by quantitative spectrographic analysis, one showed a total copper density of 6×10^{18} cm^{-3} while two contained over 6×10^{19} copper atoms/cm^3, though the electrical behavior of all three samples was quite similar.[17]

Appreciable carrier freezeout was observed in these diodes as the temperature was lowered, resulting in a large increase of the series resistance. The diodes which showed negative resistance produced no measurable light emission. The emission spectrum of the others resembled that of diodes of type II.

6. ac MEASUREMENTS

Capacitance and conductance as a function of bias voltage were measured on a Boonton bridge at several frequencies and temperatures for diodes of all three types. Typical data are shown in Figs. 10 and 11.

Data for two diodes from the same zinc diffusion, one with copper (type I) and one without, are plotted in Fig. 10. We show the cube of the reciprocal of the capacitance per unit area $(1/C)^3$ as a function of applied voltage. At forward and small reverse bias the deviations of the curves from a straight line (expected for a linearly graded junction without traps) is attributed to the presence of traps—the negative curvature observed for the copper-free diode resulting from the effects of residual deep traps (not copper) and the positive curvature for the copper-doped diodes resulting from the more shallow copper level. A comparison of the slopes of the curves reveals that the grading has not been appreciably changed, though the intercept voltage V_0 has been reduced by the copper diffusion. Very little change of capacitance with changes in measuring frequency between 5 and 500 kc was observed for these diodes. The grading deduced from the slopes of the curves is about 0.7×10^{23} cm^{-4}.

TABLE I. Line shapes of emission spectra for copper-doped diodes, giving the peak energy E_0 in eV, the widths δE at half-maximum in meV, and the asymmetry defined in Sec. 7. The values of E_0 for line 1 are the high-current limits. Data from type II diodes are given in parentheses. Line 2 was observed in type I diodes only at low temperature and current.

	4.2°K			77°K		200°K	296°K
$T=$ No.	E_0 (eV)	δE (meV)	Asym	E_0 (eV)	δE (meV)	E_0 (eV)	E_0 (eV)
1	1.47	24	−0.21	1.46	57	1.42	1.38
2 (I)				1.33	120		
2 (II)				(1.35)	(95)	(1.32)	(1.29)
3	1.29	148	−0.09	1.28	146	1.26	1.22
4	1.06	75	+0.30	1.07		1.08	1.07
5	1.00	75	−0.30	0.99		0.98	0.96
6							0.84

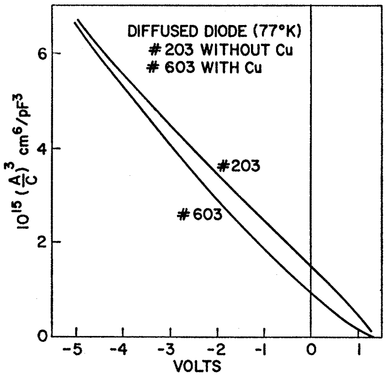

FIG. 10. The variation of capacitance with voltage for a type I diode (603) and for a similar diode having no added copper (203).

Figure 11 shows similar curves drawn from measurements made at room temperature at several frequencies on a (type II) diode having copper as the only added acceptor. In the limit of zero frequency, the reciprocal of C, the capacitance per unit area, varies as

$$1/C=6.3\times10^{-6}(0.57-V)^{1/3}\text{pF}^{-1}$$

from which the grading is found to be $a=2.5\times10^{23}$ cm^{-4} (or 1.25×10^{23} cm^{-4} for double acceptors). At higher frequencies, the curves of $1/C$ versus $(0.57-V)^{1/3}$ are displaced upwards by an amount which approaches 2.6×10^{-6} at high frequency and decrease their slope by a factor of 2 above a certain critical voltage, which varies from $V=0.5$ at 5 kc/sec to $V=-0.9$ at 500 kc/sec. Measurements at low temperatures could not be made because of the freezeout of the holes in the compensated p-region.

The electrical behavior of the type III diodes was quite complex and will be discussed in a later publication.

7. LINE SHAPES

We summarize in Table I some of the average characteristics observed in emission spectra of diodes containing copper (types I and II). The emission peaks are

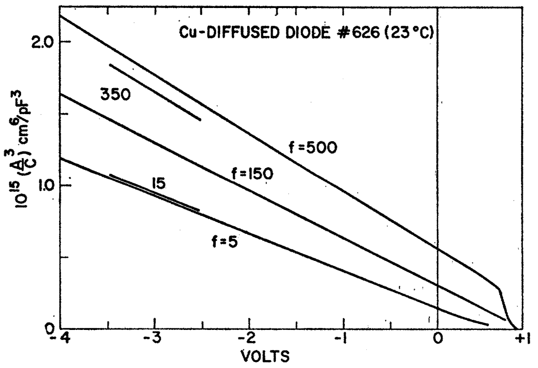

FIG. 11. The variation of capacitance with voltage and measuring frequency for a type II diode. Frequency is in kc/sec.

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[16] The Hall and resistivity measurements between 77 and 600°K were kindly performed by J. F. Woods.

[17] Quantitative spectrographic analysis of these samples was made by W. Reuter.

TABLE II. The first three calculated moments of the potential density function at low temperature near a graded junction in GaAs. The background donor density is 2×10^{18} cm^{-3}, and the carrier density assumed for the first and third lines is 10^{17} cm^{-3}. All energies are in meV.

Position	$\bar{E}$	$\langle(E-\bar{E})^2\rangle_{\text{av}}$	$\langle(E-\bar{E})^3\rangle_{\text{av}}$
p side (10^{17})	1	$(28)^2$	$(10)^3$
Junction	0	$(70)^2$	0
n side (10^{17})	-3	$(48)^2$	$-(10)^3$

listed in order of decreasing energy and are numbered consecutively for convenience in the discussion. The energy of the emission maximum E_0 is given for each temperature at which the line was observed. The width and asymmetry are given only for low temperatures because of the difficulty of resolving the thermally broadened lines at higher temperatures. The line shapes are described in terms of the energies of half-maximum —E_+ on the high-energy side and E_- on the low-energy side of the peak E_0. The width is defined as $\delta E=E_+-E_-$ and the asymmetry as $\text{Asym}=[(E_+-E_0)-(E_0-E_-)]/\delta E$. In order to understand the significance of these line shapes we must consider first the distribution of energy levels expected for a deep center in heavily doped material.

In the next two sections we outline the theory needed to interpret these spectra—the theory of the broadening of energy bands and emission spectra in impure materials in Sec. 8 and the theory of the distribution of copper acceptors and donors diffused across a p-n junction in Sec. 9.

8. POTENTIAL FLUCTUATIONS

A semiconductor crystal is, on the average, electrically neutral. However, as the charges—consisting of fixed ions and mobile carriers—are not uniformly distributed, they produce fluctuations in the local Coulomb potentials and displace the energy levels of electrons trapped on impurities. Although the complete energy density function for these fluctuations is difficult to evaluate,[18,19] its moments may be easily determined for a random distribution of ions by use of its generating function.[19] If $v(r)$ is the potential energy produced by a singly charged positive ion at a distance r, the first three moments are found to depend on the densities N_i and charges Z_i of the various types of ions as:

$$\bar{E}=-\sum_i N_i Z_i^3 \int v^3(r)d\tau\,,$$

$$\langle(E-\bar{E})^2\rangle_{\text{av}}=\sum_i N_i Z_i^2 \int v^2(r)d\tau=\sigma^2\,,$$

and

$$\langle(E-\bar{E})^3\rangle_{\text{av}}=-\sum_i N_i Z_i^3 \int v^3(r)d\tau\,,$$

where the integrations extend over all space outside of the radius of the nearest lattice site available to an ion.

The material used in making type I diodes contained 2×10^{18} shallow donors/cm^3 ($Z=+1$), about the same number of shallow acceptors ($Z=-1$) at the junction and a smaller number of copper ions ($Z=+1, -1, -2$). The ion gradient as determined by capacitance measurements was about 7×10^{22} cm^{-4}. We shall evaluate the above expressions using for $v(r)$ a screened Coulomb potential energy $v(r)=(q^2/Kr)\exp(-r/\lambda)$ where $K=12.5$, $\lambda^{-2}=6\pi nq^2/KE_f$, and the Fermi energy is determined by the carrier density n and the effective mass m^*, $E_f=(\hbar^2/2m^*)(3\pi^2 n)^{2/3}$. We assume $m^*=0.072m$ for electrons and $0.68m$ for holes.[20] If we neglect the copper ions in these expressions, we calculate the values shown in Table II for the first three moments of the energy density function at three points near the junction: on the p side assuming $p=10^{17}$ cm^{-3}($\lambda_p=2.3\times 10^{-7}$ cm), at a point within the space charge region assuming a width $w=10^{-6}$ cm, and on the n side assuming $n=10^{17}$ cm^{-3}($\lambda_n=7\times 10^{-7}$ cm). The first and third moments are small at the point within the junction because the nearly equal densities of positive and negative ions make contributions of opposite sign. The second moment, however, is large as the charge contributes as the square and the effective screening length is increased by the width w of the space charge region, $\lambda^*\approx w+\frac{1}{2}(\lambda_n+\lambda_p)$. Not included in Table II are the effects of the doubly charged copper ions, which are present where the Fermi level lies above the second substitutional copper level, and make fourfold and eightfold contributions to the second and third moments, respectively.

Thus all electronic energy levels are broadened into bands whose shapes are approximately Gaussian but may be skewed toward high or low electron energies. The widths at half-maximum, where $(E-\bar{E})^2\approx 2\sigma^2\ln 2$, are given approximately by 2.4σ or 67, 168, and 115 MeV, respectively, for the entries of Table II. The widths calculated for the type II diodes are slightly lower because of the lower substrate doping (10^{18}). If the electrons or holes were captured into one of these bands from a narrow range of states, say near the Fermi level, at a rate which was uniform over the entire band, the emission spectrum would duplicate the shape of the band. In reality the carrier densities and capture rates may be sensitive to the local Coulomb potential so that one part of such an energy distribution is favored and the emission line is modified. Some of these modifications are discussed below. The shape of the emission line at low temperature, however, is still related to that of the level distribution and can provide useful information.

In particular, a line skewed toward low energy corresponds to the capture of an electron if the process occurs on the p side of the junction ($\sum_i N_i Z_i^3<0$) and to the capture of a hole if it occurs on the n side ($\sum_i N_i Z_i^3>0$).

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[18] E. O. Kane, Phys. Rev. **131**, 79 (1963).

[19] T. N. Morgan (unpublished).

[20] H. Ehrenreich, Phys. Rev. **120**, 1951 (1961).

Conversely, a line skewed toward high energy involves an electron on the *n* side or a hole on the *p* side. In addition, a broad peak (half-width > 100 meV) is emitted largely in the vicinity of the junction while a narrow peak probably originates outside of the junction. Thus, of the lines in Table I the wider ones, number 3 and probably number 2, arise within or near the space charge region. Number 4 is from either capture of an electron on the *n* side or of a hole on the *p* side of the junction, while number 5 is from a carrier of opposite sign or on the opposite side of the junction from 4. Line 6 is too poorly resolved to analyze in this way and line 1, the band-edge peak, is discussed below.

9. COPPER DISTRIBUTION

Further information on these transitions can be gleaned from a knowledge of the diffusion process of copper in GaAs.[7] Capacitance measurements and photomicrographs of the junction region in type I diodes before and after copper diffusion indicate that although the copper has penetrated beyond the junction region, it is present in low concentrations—probably less than 10^{17} cm^{-3}—so that, though the diffusion occurred at a high temperature, the copper density did not reach its equilibrium value. The copper diffusion proceeds rapidly through an interstitial mechanism. As the interstitial form is known to be a single donor and substitutional copper a double acceptor,[7] the total equilibrium concentrations of both species and hence their ratio are strongly dependent on the position of the Fermi level during diffusion. For example, a low density of copper diffused through a junction at 1000°C will distribute itself between substitutional and interstitial sites with the ratios shown in Fig. 12.[21] If diffusion (or annealing) occurs at a lower temperature, this ratio will change even more dramatically between the *n* and *p* sides. At the measuring temperature the Fermi levels (we use the term Fermi level under nonequilibrium conditions to mean the quasi-Fermi level appropriate to the distribution under consideration) lie below both substitutional copper levels on the *p* side and also, at high forward bias, throughout much of the space charge region, so that only the neutral center is present in sufficient density to be seen. Conversely, on the *n* side, only the doubly ionized copper is seen.

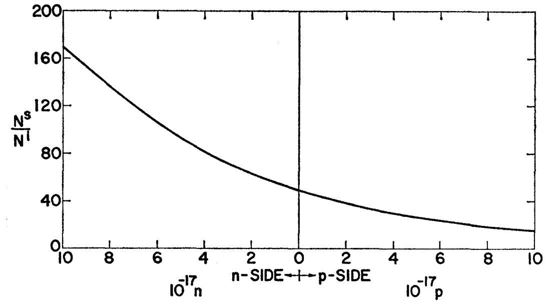

FIG. 12. The equilibrium ratio of substitutional to interstitial copper at low copper density as a function of the net substrate doping.

10. IMPURITY LINES FROM TYPE I DIODES

In this and the following section we interpret the impurity emission spectra of diodes of types I and II with the help of the two preceding sections. The band-edge line is analyzed in Sec. 12 in terms of a tunneling model, and the voltage dependence of the emission intensities of all lines is interpreted in Sec. 13.

The discussion of Sec. 9 shows that the capture of an electron on neutral copper occurs principally within the junction region and produces a broad, nearly symmetrical line—number 3 at 1.29 eV. The difference between this energy and the energy E_1 of the high-current band-edge line gives a value at low temperature of $E_3-E_v=0.18$ eV, approximately 0.02 eV higher than the mean thermally determined activation energy[16] of the homogeneous copper-doped material. The activation energy is discussed in Sec. 17. (In this discussion E_v and E_c represent the effective valence and conduction band-edge energies as they contribute to recombination.)

Similarly, the capture of an electron by the singly ionized substitutional copper center will occur principally on the *n* side of the junction, where recombination occurs by hole capture on the Cu^{--} centers and electron capture on the Cu^{-}, and produce a line of medium width skewed toward high energy, line number 4 at 1.06 eV. Comparison of this with E_1 gives an energy (at 4.2°K) $E_4-E_v=0.41$ eV, close to the value (0.42 eV) reported by Blanc *et al.*[2]

The capture of a hole by the low density of interstitial copper occurring near the junction should produce a broad weak line (skewed slightly toward high energies if the transition rate in the *p* region is sufficiently large), and shifted toward low energy according to the position of the Fermi level in the partially filled band of states. Line number 2 agrees with this description and its location, 1.33 eV at 77°K, places its Fermi level near $E_c-E_{f2}=0.13$ eV.

The fact that line 5 is approximately a mirror image of line 4 (equal in width but skewed toward low energy) suggests that it is produced by the capture of a hole on a center lying about 0.50 eV below the conduction band principally on the *n* side of the junction, possibly associated with a vacancy. It may be the same center observed by capacitance and luminescence measurements in these diodes before the copper diffusion.

The agreement between the computed band shapes and the observed line shapes at low temperatures indi-

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[21] These values were deduced from Hall and Racette (Ref. 7). We have included the electron degeneracies g_i in computing the ratios of ionized to un-ionized centers, though these were omitted in the paper cited and in their Ref. 20 (Shockley and Moll). We have used for interstitial copper $g_1=2$ and for substitutional, $g_{-1}=\frac{1}{3}$ and $g_{-2}=\frac{1}{8}$.

cates that the capture rates are not strongly sensitive to the local potential and suggests that the ease with which electrons and (light) holes can tunnel into potential barriers enables the carriers of both signs to reach essentially all regions of the crystal.

At higher temperatures, where the tunneling processes become unimportant compared to the recombination of thermally generated carriers, the line shapes and positions depend upon the spread of the carrier distribution and upon the energy dependence of the capture rates. This is particularly evident for the 1.06-eV line, number 4. In Fig. 13, we show the temperature dependence of the energy levels as derived from the peaks of the emission lines. Number 4 (solid line), which is striking in that its energy decreases markedly with increasing temperature, is produced by the capture of electrons on negatively charged (repulsive) centers. Because of the repulsive Coulomb force, the incident electron must penetrate a potential barrier to be captured by the short-range attractive potential near the core, and its capture probability will increase with increasing kinetic energy. If this capture probability varies approximately as E^n with n positive, the most probable energy for capture from a Maxwellian distribution at a temperature T occurs near nkT, and the peak energy is shifted to higher energy by that amount. For this case, the corrected values of the trap energy are given by $E_4-E_v=E_1-E_{\mathrm{peak}}+nkT$. A choice of $n=4.0$ for line 4 gives a binding energy $E_4-E_v=0.41$ eV at all temperatures (drawn as a dashed line in the figure). Capture by neutral or attractive centers occurs without this shift in energy as the cross sections generally decrease with increasing energy.[22] Some variation of capture rate, however, with changes in the local Coulomb potential is expected and may cause a shift in the energy of the emission peak. It is significant to note that if the capture rate varies exponentially with energy, it introduces a shift in the peak of a Gaussian emission line without altering its width. Thus, the level energies deduced from the spectra must be considered approximate.

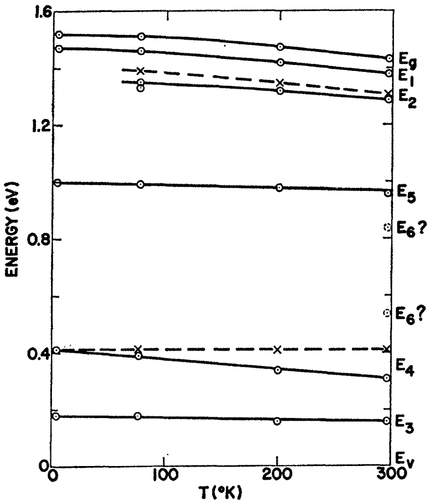

FIG. 13. The temperature dependence of the energy levels deduced from the positions and shapes of the emission lines. The subscripts E_1 through E_6 identify the levels with the corresponding emission lines in Table I. All energies are referred to the valence band edge E_v and the band gap in pure material E_g is shown for comparison. The crosses and dashed lines are corrected as discussed in the text.

Similarly the position of the Fermi level within a partially filled band influences the peak position, though this may also alter the shape. The donor level producing line 2 is an example of such a partially filled band as is probably to a lesser degree the first acceptor level. In the latter case the filling of the lower states in the band could produce a small shift of the emission energy of line 3 toward lower energies. The binding energy of the donor level has been estimated to be $E_c-E_2=0.07$ eV from the variation of the energy of line 2 with temperature in type II diodes, assuming the distribution to be Gaussian and the position of the Fermi level constant. This rather high value for the binding energy suggests that the electron wave function is strongly perturbed by the copper core.

The small variation of the energy E_5 shown in Fig. 13 is probably reasonable for a center lying 0.5 eV below the conduction band.

11. IMPURITY LINES, TYPE II

The room-temperature emission spectra from type II diodes are, as expected, similar to those from type I except that the impurity lines are much stronger, and the band-edge line is too weak to be observed. As the density of interstitial copper donors near the junction is estimated to be $N^i=10^{17}$ cm^{-3},[21] and the activation energy is near 0.08 eV, the number of occupied donor sites is about 10 times the number of free electrons in the conduction band at 300°K, and line 2, near 1.29 eV, becomes the dominant peak. Most of this emission occurs near the p side of the junction, as the hole density within the junction (between x_1 and x_2) does not rise much above its low-current value of $p\approx 2\times 10^{11}$ cm^{-3} (see Fig. 14). Lines 3 near 1.22 eV and 4 near 1.07 eV are less intense, as the junction region contains so few holes, and the donors dominate the recombination on the p side, where both holes and electrons are present.

At 200°K, these effects are exaggerated: Line 3 disappears, indicating that virtually all electrons injected into the p region are trapped by the donors, and line 4 becomes quite weak. The persistence of line 5 at this temperature is consistent with the transition proposed above—the capture of a hole on a center lying about 0.5 eV below the conduction band—and the wide symmetrical lines are reasonable for transitions occurring in a region containing only singly ionized centers and few free carriers.

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[22] M. Lax, J. Phys. Chem. Solids 8, 66 (1959).

To understand the low-temperature luminescence, we must consider the widths of the impurity levels in the copper-doped p region. We expect the donor density to be about 10^{18}Te/cm^3 plus a smaller amount of interstitial copper, $N^i=1$ to 5×10^{17} cm^{-3} and the acceptor density to be $N^s\approx7\times10^{18}$ cm^{-3}.[21] Of these acceptors, only a part $n^s\approx10^{18}$ cm^{-3} are ionized by the electrons released by the donors. As the density of free electrons and holes is very small, the screening is provided in part by the carriers trapped in the donor and acceptor bands. Such screening is relatively ineffective, as the electron positions are restricted to the available impurity sites.[19] Thus, the energy levels are very broad and the Fermi levels lie well below the mean band energies. For example, in the acceptor band (assumed to be Gaussian) near the junction, where only one-seventh of the levels are occupied, the Fermi level lies 1.07σ below the mean energy $\bar{E}=0.18$ eV deduced from the emission peaks, with the variance given by $\sigma^2=\langle(E-\bar{E})^2\rangle_{\text{av}}$ as computed above. It is this proximity of the Fermi level and the valence band which reduces the freezeout of holes and permits the luminescence to persist at low temperature.

To explain the disappearance at 77°K of all impurity lines other than line 2, we must assume that the product of the free electron and hole densities becomes negligible throughout the diode. Thus on the n side and in the junction, where there may be a nonzero electron density, there must be few holes, free or trapped, to complete the recombination process, while on the p side where free holes may be present the injected electrons must be trapped on the donor level. (The small amount of band-edge emission observed under certain conditions could be generated at the boundary between these two regions.) Under these limitations the flow of electron current in the p region must take place through a donor impurity band and current flow may occur without emitting light. The measured value of the external quantum efficiency $\eta_{\text{ext}}=2\times10^{-4}$ can be used to obtain a lower limit for the hole density needed to emit the observed light intensity. The radiative current is proportional to the density of occupied copper donor levels (assumed half-full) $n^i\approx2\times10^{17}$ cm^{-3}, the capture cross section $A\approx10^{-13}$ cm^2, the thermal velocity $v=10^7$ cm/sec, the hole density p, the volume of the radiating region $V=6\times10^{-8}$ cm^3 for a typical diode, and the electronic charge. By equating this current to η_{ext} times a current of 100 mA, we find a value of $p=5\times10^{13}$ cm^{-3} as an approximate lower limit for the hole density. To see that this is a reasonable value, we compute the resistance it predicts for the p region and find that for a mobility of 200 cm^2/V-sec the predicted resistance is only a factor of 2 above the value measured at low currents $R=6500\ \Omega$. Using this value of the hole density, we find the Fermi level to be 10.5 $kT=0.07$ eV above the edge of the valence band or 0.11 eV below the average acceptor energy if the tail in the valence band density of states is neglected. By equating this energy to the result obtained above, $1.07\sigma=0.11$ eV, we find for σ a lower limit of $\sigma>100$ meV, though this value would be reduced by consideration of the band tails.

We can now use this model to understand the emission spectra and breakdown at 77°K. Electrons are injected across the junction into the donor band where their Fermi level lies well below the mean donor binding energy and hence many kT below the conduction band. Consequently, there are no free electrons present to recombine with the trapped holes, and recombination occurs between free holes and the electrons in the donor band. The emission peak is narrower than the impurity bands as the higher energy donor states are not occupied by electrons. Conduction of current from the electrode to the junction passes through both the donor and valence bands though undoubtedly with a higher mobility in the valence band. As the current is increased, the distribution of trapped electrons increases in density and moves further toward the positive electrode causing a corresponding increase in the hole density and reducing the resistance as shown in Fig. 7.

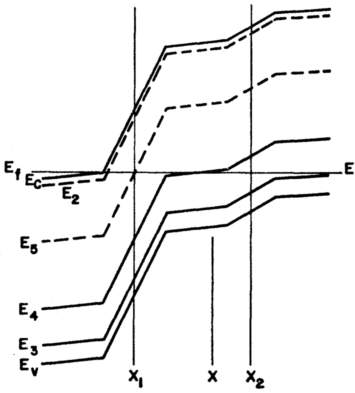

FIG. 14. The configuration of energy levels across a type II junction at zero bias. The Fermi level is E_f and the other levels are identified as in Fig. 13. The centers represented by the dashed lines are assumed to occur in low concentrations.

12. BAND-EDGE EMISSION

Line 1, the band-edge line, is much narrower than the impurity lines, as it is produced by transitions between states near the Fermi levels in the two bands regardless of the local potential fluctuations. The fact that the electron and hole distributions do not overlap in space—except at high currents—demands that the recombination proceed by tunneling. This accounts for the "peak shift" observed in these diodes, as a tunneling electron near the electron Fermi level recombines in the space-charge region with a tunneling (light) hole near its Fermi level with the emission of a photon whose energy, in electron volts, is given very nearly by the voltage applied across the junction. This photon-assisted tunneling process has been discussed by Pankove[23] and by Archer *et al.*[24] The dependence upon voltage of the

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

[24] R. J. Archer, R. C. C. Leite, A. Yariv, S. P. S. Porto, and J. M. Whelan, Phys. Rev. Letters **10**, 483 (1963). In contrast to their interpretation, our analysis of band-to-band tunneling gives agreement with their high-voltage data, their region B, and attributes the smaller slope at lower voltages to impurity effects.

recombination rates calculated with this model agree well with the measured values for the edge emission intensity,[25] and the predicted line shapes and energies are close to those observed. Using this model the line width for type I diodes has been computed to be approximately 14 meV below about 30°K.[25] The lines measured at helium temperature have widths of about twice this value—24 meV—and exhibit tails which decrease exponentially toward low energy. The latter appear to arise from energy loss through nonradiative processes.

At higher temperatures the tail of the Fermi distribution permits transitions between states separated by energies greater than V (in electron volts) with a corresponding increase in the tunneling probability. Thus, at 77°K, the peak moves to higher energy and the width is calculated to be about 60 meV for an applied voltage of 0.10 V below the effective band gap (in eV) in agreement with experiment.

13. RELATIVE EMISSION INTENSITIES

The voltage dependence of the intensities of the various lines can be understood in terms of the recombination statistics of the impurity centers.[26] At high temperature and for low values of applied voltage V the intensity of each line varies approximately as $\exp(qV/kT)$ which, for the impurity lines, changes to $\exp(qV/2kT)$ at a critical voltage $V=V_k$ which is approximately twice the energy of the center as measured from midgap. This is seen in Fig. 4 where $V_k=1.11$ V for the 1.21-eV line and lies below 0.96 V for the 0.96-eV line. The kink at 1.09 V in the 0.96-eV curve and the one at 1.24 V in the 1.22-eV curve occur where the region of maximum recombination in the junction coincides with the edge of the space charge region. The low value 1.09 V for this kink in the 0.96-eV curve identifies the corresponding center as a donor lying in the upper half of the gap (cf. the discussion in Ref. 26). Thus, the emission intensity from the deeper traps changes slope at lower values of bias voltage and emission in the high-energy lines is favored at high current. At low temperatures, tunneling replaces thermal excitation of the carriers, but the results are qualitatively the same. The variation of these intensities with diode current is complicated by the fact that several processes can contribute to the current, but becomes fairly simple in the range of low or high current as shown in Fig. 1.

14. NONRADIATIVE RECOMBINATION

The absence of emission below about 0.8 eV (at least down to 0.4 eV) and the smallness of the measured quantum efficiencies in these diodes strongly suggest that a large fraction of the transitions occurs nonradiatively—particularly between states whose energies differ by less than 0.8 eV. A mechanism for this nonradiative recombination is readily constructed from the model of energy levels developed above. As the broad bands of impurity states span the entire energy gap between the conduction and valence band tails they provide states through which electrons may pass by successive emission of low-energy phonons. Tunneling transitions between defects in different parts of the crystal complete the process. The probability that an electron follow such a sequence of n steps is roughly proportional to the nth power of the probability of one step, while the number of steps increases with the energy difference between the initial and final states. Consequently, the probability of the resulting recombination process decreases approximately exponentially with the amount of energy to be dissipated (other factors being equal) in contrast to a radiative process whose probability is essentially independent of photon energy. This process is most important at high temperatures in materials containing high densities of gap states broadened by high ion densities, a conclusion supported by comparison of our copper-doped diodes with normal laser diodes.

15. CAPACITANCE OF TYPE I DIODES

In this and the succeeding section the capacitance and ac conductance of diodes of types I and II are interpreted in terms of the role played by deep traps in alternating current flow through p-n junctions. A brief discussion of type III diodes is given in the final section.

The variation of capacitance with bias voltage for diodes containing deep traps is quite complicated and will be discussed in a separate publication.[27] Only the conclusions pertinent to these diodes will be outlined here. If the diodes were simple diffused junctions without deep centers, the curves of Fig. 10 showing $(1/C)^3$ versus V would be nearly straight lines curving upwards slightly at high reverse bias where the nonlinear grading becomes important. The slope of the linear portion is determined by the ion gradient a at the junction. A similar diode containing a low density N of deep traps which can adjust their Fermi level to the changing bias, but cannot follow the ac measuring signal appears as two capacitors in series: one equivalent to the diode without the traps (though with a reduced voltage intercept V_0) and the other a voltage-independent capacitor of width $w=N/2a$.

The copper-free diode, number 203, plotted in Fig. 10 shows this type of curve with $a=7\times10^{22}$ cm^{-4} and $N\approx4\times10^{17}$ cm^{-3} while the copper-doped diode does not. We thus conclude that the diodes made without copper contained deep traps which are not associated with the presence of copper, but that the recombination through these centers occurs with small radiative efficiency. (They produced weak emission peaks at 300°K.) Such centers are known from capacitance measurements to be common in laser-type diodes, frequently in sufficient

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[25] M. I. Nathan and T. N. Morgan (unpublished).

[26] T. N. Morgan, Solid State Device Conference, Boulder, 1964 (unpublished report).

[27] T. N. Morgan (unpublished).

density to show emission at low temperatures in a peak near 1.00 eV.[28] If the traps lie sufficiently close to a band edge for their Fermi level to follow the applied signal, the curvature of the $(1/C)^3$ versus V curve is reversed at forward bias in agreement with the curve in Fig. 10 for diode number 603 containing copper.

16. CAPACITANCE OF TYPE II DIODES

In diodes of type II, the junction is formed between an n-type region containing a relatively small amount of copper (principally in substitutional sites) and a heavily copper-doped p region in which the interstitial copper density is relatively high (equilibrium values for diffusion at 1060°C are approximately $N^i=4\times10^{17}$ and $N^s=6.4\times10^{18}$ cm^{-3}).[21] The rapid diffusion through motion of the interstitial form in the p region compared to the slower diffusion in the n region determines the steep diffusion front and grading in the junction,[29] $a=1.3\times10^{23}$ cm^{-4} for double acceptors.

In Fig. 14, we sketch the equilibrium band edges and energy levels found in the vicinity of the junction in these diodes. The levels are identified by the numbers of the emission lines they produce. The pinning of the Fermi level at the second acceptor level can cause the space charge to divide into two parts as shown in the figure. The left-hand (n-side) junction is centered around the position x_1 where the doubly ionized acceptors neutralize the charges of the donors, $2N^s(x_1)=n_0+N^i(x_1)$. The right-hand junction, near the p side, is centered around x_2, where the acceptors are only singly ionized, $N^s(x_2)=n_0N^i(x_2)$. Thus, if we assume linear acceptor grading, $N^s=N_0{}^s+ax$, and neglect the small amount of interstitial copper in the vicinity of the junctions, we find for the distance between the two junctions $x_2-x_1=n_0/2a\approx4\times10^{-6}$ cm, for $n_0=10^{18}$ cm^{-3}. The region between x_1 and x_2 is divided between the space-charge regions of the two junctions and a neutral region (of finite conductivity increasing toward the right) in which the second acceptor level is partially full. The capacitance-voltage curve of such a diode is quite complex[27] and will not be discussed in detail here. In brief, the combination of the conduction and displacement currents in such a diode adequately explains observed variation of capacitance with bias and frequency (Fig. 11) and gives an estimate of the distance between junctions $x_2-x_1=3.9\times10^{-6}$ cm, in agreement with the value calculated above. In addition, the high-frequency measurements indicate the presence of a capacitor of effective width $w=2.9\times10^{-6}$ cm in series with the diode represented in Fig. 14. This series capacitance together with the smallness of the built-in potential $V_0=0.57$ V may be produced by the interstitial and other centers present in the junction region.[27]

17. TYPE III DIODES

We shall discuss in this section only those results obtained for type III diodes which have bearing on the properties of the copper centers in diodes of types I and II.

The Hall-effect measurements made on several diffused samples from which diodes were fabricated imply unreasonably high densities of copper acceptors $N_s\approx5\times10^{19}$ cm^{-3} for an activation energy of 0.18 eV and a g factor of $\frac{1}{3}$, if[30,31] the usual model of a well-defined copper level and normal valence band structure is assumed. In addition, the activation energies measured differed for different samples and depended on their thermal history.[31] These effects are consequences of the fluctuations in local potential discussed above and originate in part from the tail on the valence band[18] and, in part, from the breadth of the band of impurity states. Because of the latter effect, the position of the Fermi level within the copper acceptor band depends upon the fraction n_s/N_s of the centers which contain electrons, and the activation energy (measured at not too high temperatures) can vary widely between samples.

The negative resistance observed in these diodes above 0.3 V forward bias, Fig. 9, indicates that an appreciable tunneling rate exists between the conduction band and the deep-lying copper levels.[32] (In normal n^+-p^+ tunnel diodes the peak occurs near 0.1-V bias.) Our electrical measurements supporting this model will be discussed in a subsequent paper.

ACKNOWLEDGMENTS

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[28] M. I. Nathan, G. Burns, S. E. Blum, and J. C. Marinace, Phys. Rev. **132**, 1482 (1963).

[29] L. R. Weisberg and J. Blanc, Phys. Rev. **131**, 1548 (1963).

[30] J. Blanc and L. R. Weissberg, J. Phys. Chem. Solids **25**, 221 (1964). Their degeneracy parameter is the reciprocal of the usual electron degeneracy ratio g as it appears in the trap Fermi function, $f=[1+(1/g)\exp(E-E_f)]^{-1}$. A choice of 3 which is consistent with their data corresponds to a value $g=\frac{1}{3}$.

[31] One of the samples heated to 700°K during Hall measurements suffered an irreversible change and when remeasured showed an activation energy below 300°K of 0.175 eV.

[32] Similar processes have been discussed by Sah for gold levels in silicon. C. T. Sah, Phys. Rev. **123**, 1594 (1961).

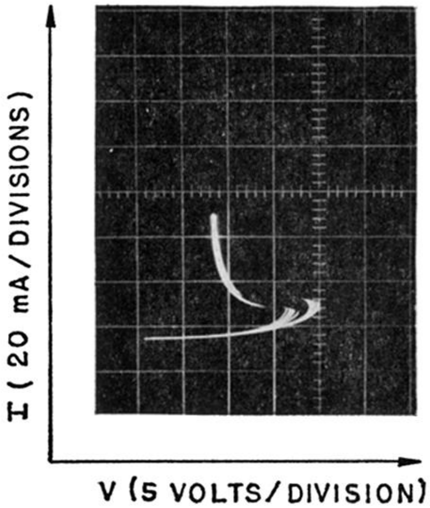

Fig. 6. Current-voltage characteristic of a type II diode at 77°K showing breakdown at high voltage.

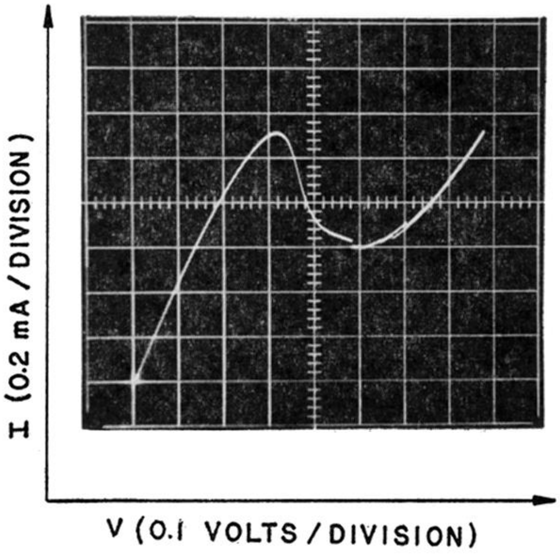

FIG. 9. Current-voltage characteristic of a type III diode at room temperature showing negative resistance (tunnel diode characteristic).