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Effects of Co⁶⁰ Gamma Irradiation on Epitaxial GaAs Laser Diodes*

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The characteristics of defects introduced in epitaxial GaAs by room-temperature Co⁶⁰ irradiation have been studied by observing the degradation of light emission from GaAs laser diodes. The luminescence degradation is indicative of a decrease in electron lifetime in the *p*-type region brought about by the introduction of nonradiative recombination centers. These defects anneal in a single stage centered at 237°C. Isothermal-annealing studies show that the defects anneal by a first-order kinetic process with an activation energy of 1.7 eV and a preexponential factor of 10¹³ sec⁻¹. The annealing properties of the defect suggest that it is a complex whose dissociation is the limiting step in the recovery process. The defects can also anneal at temperatures as low as 76 °K under the influence of a strong forward bias. A dc forward bias at 2.2×10² A/cm² at room temperature for 1 h produces complete recovery of the light intensity. The possibility of annealing due to heating while under strong forward bias has been considered and does not appear to be responsible for the bias annealing. Rather, the forward-bias-induced recovery is thought to be due to an increase in the probability of annihilation because of a change in charge state of the defect complex following capture of a minority carrier. The various aspects of forward-bias annealing observed in this study can be explained by this model. On the basis of the above results, the complex has been tentatively identified as consisting of an impurity and an As interstitial.

INTRODUCTION

The luminescence emitted from GaAs because of various forms of excitation has been the subject of intensive study during recent years. The effects of radiation on GaAs luminescence have received less attention. With the exception of a few papers on photoluminescence and cathodoluminescence,¹⁻⁵ radiation effects investigations have concentrated on electroluminescence, especially in light-emitting diodes.⁶ Aukerman and co-workers have extensively studied electron-irradiated GaAs diodes.⁷⁻¹⁰ The primary aim of these latter investi-

gations was to use radiation as a tool for discovering the mode of operation of light-emitting diodes. For example, it was shown that the electroluminescence can be due to either recombination of electrons injected into the *p*-type side of the diode or recombination in the depletion region according to a "band-filling" model. The predominance of either type of recombination depends on such parameters as doping level, temperature, and forward-bias voltage. In other studies, Saji and Inuishi¹¹ have shown that Co⁶⁰ irradiation increases the threshold current of laser diodes at 77 °K, while Petree¹² found a degradation threshold for neutron

irradiation at approximately 10^{12} neutrons/cm². Compton and Cesena¹³ have also studied the decrease in light output with irradiation. Following electron irradiation, they observed no thermal annealing below 100 °C, but were able to remove the damage by heavily forward biasing the diodes at room temperature.

In this paper, studies of both forward-bias annealing and thermal annealing of electroluminescence in Co⁶⁰-irradiated epitaxial laser diodes are reported.

EXPERIMENTAL PROCEDURE

The diodes used in this investigation were obtained from RCA. A *p*-type layer doped with 3.7×10^{19} -cm⁻³ Zn was deposited by liquid epitaxy on a Si-doped (3.4×10^{18} cm⁻³) *n*-type substrate. The junction was formed by diffusing the Zn into the substrate about 3 μ below the metallurgical junction. The diodes had a cross section of 3×12 mils. All of the diodes examined in this study were manufactured from the same GaAs wafer. Glass windows ordinarily supplied with the diodes were removed.

Depending upon the particular measurement being made, the laser diodes were driven in either one of two ways. In the simplest method, the diode was driven by a Tektronix curve tracer or a PAR reference voltage source, and the output was detected with an RCA 7102 photomultiplier having S-1 response. In this case the maximum allowable current was 50 mA (2.2×10^2 A/cm²). For the majority of measurements, the reference channel of a PAR lock-in amplifier was used to trigger a pulse generator that supplied 180-nsec-wide pulses at 90 Hz to the diode, which was in series with a 100- Ω current limiting resistor. The output of the 7102 photomultiplier tube was fed to the signal channel of the lock-in amplifier. The diodes were run at 5 V corresponding to a current of approximately 37 mA. The reason for operating the diodes at this low voltage will be brought out later in the paper.

Data were taken at 300 and 76 °K. At the higher temperature the diodes were placed directly in front of the photomultiplier tube window, and the tube was operated at a reduced voltage (650 V) in order to minimize the noise. A cooled photomultiplier tube operating at 1200 V was used for 76 °K measurements. In this case, the emitted light was focused on the entrance slit of a small Bausch and Lomb monochromator so that the spectrum could be observed.

Defects were introduced into the GaAs lasers by irradiating them at room temperature with the Co⁶⁰ source in the Sandia Gamma Irradiation Facility (GIF). The γ flux at the irradiation position was 3.8×10^{11} γ rays/cm² sec or in terms of

dose, 0.7 Mrad/h. The diodes were usually irradiated for 16–18 h before studying the luminescence degradation and recovery.

Thermal-annealing experiments were carried out by immersing the diodes in a 1-liter silicone oil bath which was located inside a small furnace. An access hole in the top of the furnace allowed one to plunge the diode into the oil without disturbing the furnace. At the end of each anneal, the diodes were quenched and washed in trichloroethylene.

Forward-bias annealing was accomplished in two ways. For pulsed annealing, a Velonex high-voltage pulse generator was used to supply pulses a few microseconds in width and several hundred volts in magnitude. Continuous annealing was carried out by operating the diodes on a curve tracer or the PAR voltage source. Injection annealing was attempted at temperatures ranging from 76 to 300 °K. At intermediate temperatures, a thermocouple was soldered to the diode case and cold nitrogen gas was passed over the diode.

During the course of the measurements, one diode was used as a standard in order to compensate for any fluctuations in the measurement apparatus. Unirradiated diodes were subjected to thermal- and forward-bias annealing conditions to find out if these operations brought about any degradation independent of irradiation. Heating the diodes to 275 °C in the oil bath produced no effect. However, degradation of the diodes did occur for forward-bias pulses greater than 8 A and wider than 3 μ .

EXPERIMENTAL RESULTS AND DISCUSSION

Diode Characteristics

Before studying the effects of Co⁶⁰ γ rays on the laser diodes, certain measurements were made to characterize the operation of the diodes. Figure 1 shows current-voltage curves for typical unirradiated diodes at 300 and 76 °K. Over the entire range from 0.4 A/cm² to 2.2×10^2 A/cm², the current varies exponentially with voltage at 300 °K. Calculation of the slope and intercept indicates that the current density obeys the following equation at 300 °K over the measured range:

$$J = 6.5 \times 10^{-9} e^{qV/2kT} \text{ A/cm}^2. \quad (1)$$

The factor 2 in the exponent is characteristic of current flow due to recombination within the space-charge region, a mechanism often observed in GaAs diodes and, especially, in laser diodes.¹⁴

In contrast with the *J*-*V* characteristics, Fig. 2 shows that the intensity of the light output at 300 °K varies as $e^{qV/kT}$ over several orders of magnitude. This result has two major implications. First, it may be that the proportionality to

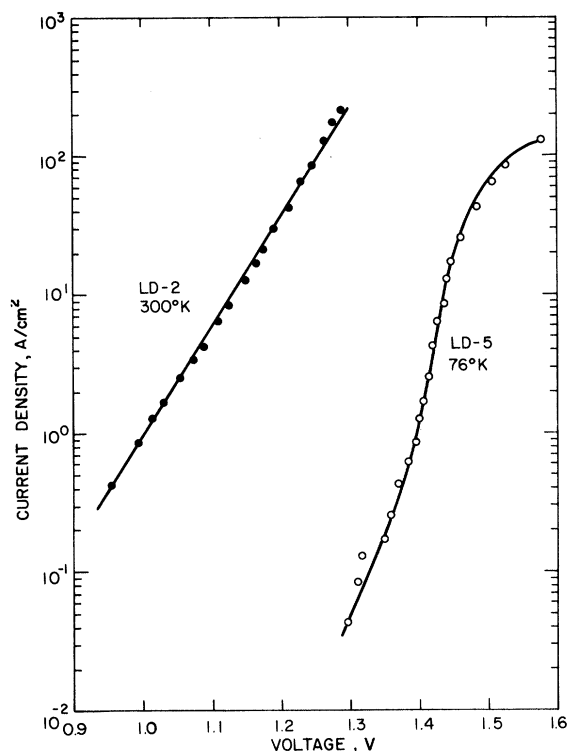


FIG. 1. Current-voltage characteristics of two typical unirradiated epitaxial GaAs laser diodes at 300 and 76°K.

$e^{qV/kT}$ is incidental and that the light intensity is merely proportional to J^2 . One would expect this result if recombination within the space-charge region was radiative and bimolecular. However, as Dean¹⁵ has recently pointed out, the above result does not constitute sufficient experimental evidence for concluding that the kinetics of radiative recombination are bimolecular. The second implication is that the intensity is proportional to $e^{qV/kT}$ because the radiative current is due to diffusion and recombination of minority carriers that have been thermally injected into the neutral region. This explanation of the radiative current is favored for two reasons. First of all, there is considerable precedent in the literature^{10,14,15} for this picture. One would expect injection luminescence to be inefficient at higher temperatures and, in fact, a superposition of two current-flow mechanisms is often observed with the majority of the current flowing by space-charge recombination. Second, additional experimental results will be presented later in this paper to support the view of a thermally injected diffusion-limited radiative current. Therefore, for the moment, we assume that this is the proper interpretation. Consequently, at 300°K the forward current in these diodes is primarily a depletion layer-recombination cur-

rent, but the small fraction of the current which flows by diffusion is responsible for the light emission.

Examination of Figs. 1 and 2 shows that the behavior at 76°K is more complex. Because of the higher voltages required at 76°K resistive losses in the neutral regions now make a significant contribution as indicated by the bending over of both low-temperature curves in Figs. 1 and 2 at high voltages. At low temperatures such as 76°K, current flow due to tunneling is often observed.¹⁴⁻¹⁹ The dependence of current and light intensity on voltage is usually still exponential, but the slope is often independent of temperature.¹⁷ The tunneling process can proceed by several mechanisms. In the band-filling model, horizontal tunneling of electrons can occur from the conduction band on the *n* side to conduction-band tail states on the *p* side with no loss of energy.¹⁸ A second tunneling mechanism which has been successfully used to explain experimental results¹⁹ is photon-assisted tunneling. In this case, the electron tunnels from the conduction band on the *n* side to the valence band on the *p* side with the simultaneous emission of a photon. For both types of tunneling the peak energy of the emission is related to the applied voltage by

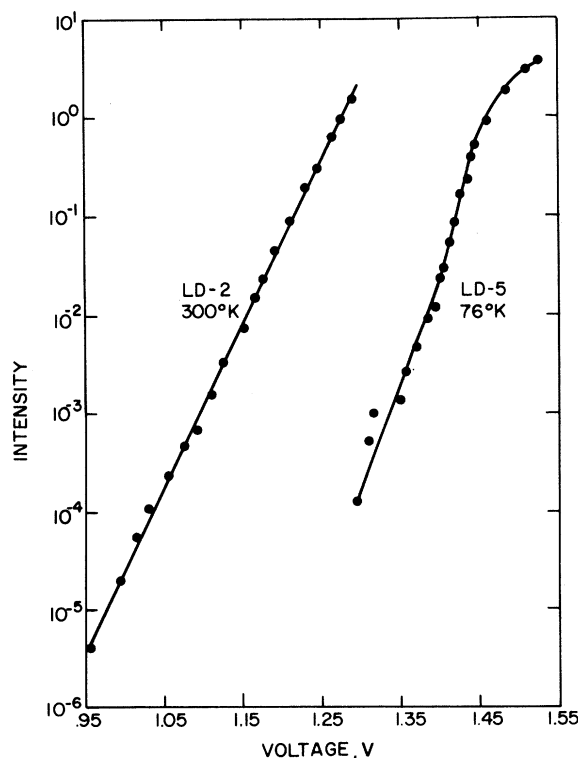


FIG. 2. Intensity of light emission versus forward-bias voltage for unirradiated laser diodes at 300 and 76°K.

$$h\nu = q(V \pm V_0) \text{ eV}, \quad (2)$$

where V_0 is of the order of millivolts. Unfortunately, we do not have enough low-temperature data to make any definitive statements about the exact mechanism of current flow. However, the shift in peak energy of the emission with forward bias was briefly measured at both 300 and 76 °K. At 76 °K, the following values were obtained: At $V = 1.440$ V, $h\nu = 1.423$ eV, and at $V = 1.492$ V, $h\nu = 1.470$ eV. The data of Fig. 1 have been used to correct the voltages for resistive losses. In accordance with a tunneling-type mechanism, $h\nu$ increases with voltage with $V_0 \approx 20$ mV. At 300 °K, no shift was observed, which agrees with diffusion-controlled light emission due to thermal injection of electrons. The presence of a bias-independent peak at 1.47 eV at 300 °K could have an alternate explanation, however. Figure 2 indicates that the emission can be observed at bias voltages as low as 0.9 V. Consequently, there is a significant difference between the emission peak and the voltage (0.6 eV). Nathan *et al.*²⁰ have invoked an Auger mechanism to account for the light emission at low temperatures (4.2 °K) and low voltages such that $h\nu - qV > 1000kT$. The Auger process is responsible for increasing the energy of the electron to the point where it can diffuse to the p side and recombine. In judging whether or not the Auger mechanism is plausible for our use at 300 °K, it is important to note that one should compare V with V_B , the built-in voltage, instead of $h\nu$ or E_{Gap} , because V_B corresponds to the potential that must be overcome by thermal excitation. At $V = V_B$ one is in the high-current regime even though $E_{Gap} - qV$ may still be greater than kT . For the diodes used in this study, V_B is about 1.2 V at 300 °K. Consequently, $V_B - V$ is approximately 0.3 V at $V = 0.9$ or, more importantly, $q(V_B - 0.9 \text{ V}) \approx 12kT$, which is much smaller than the corresponding difference at 4.2 °K. Rough calculation using the simple diode equation indicates that for parameters characteristic of our laser diodes one can expect significant forward currents (mA/cm²) at 0.9 V. Consequently, while the Auger mechanism may be important at low temperatures, it apparently does not need to be invoked at higher temperatures even though $h\nu$ is greater than qV .

Co⁶⁰-Induced Degradation

Assuming that the emitted light is due entirely to a diffusion current at 300 °K for the current levels used in these measurements, we can express the light intensity as¹⁰

$$I = C \int_0^\infty \Delta n_p N_A dx, \quad (3)$$

where C is a constant, Δn_p is the excess electron

density on the p side, and N_A is the acceptor concentration. In writing this equation, two assumptions have been made. First, it is assumed that the emitted light comes from the p -type region. The basis for this assumption is that the emission band occurs at a longer wavelength than the emission from n -type GaAs.^{14,21} In addition, previous investigations have shown that the light usually comes from the p -type region.¹⁴ The second assumption is that I is proportional to N_A . Recent work²² has demonstrated that the near-edge lasing transition is conduction band acceptor in epitaxial material and donor acceptor in bulk-grown GaAs. In either case, one would expect I to depend on N_A , assuming the acceptor involved is the dopant atom. Aukerman *et al.*¹⁰ developed Eq. (3) for a diffused junction and obtained

$$I = C' D_n \tau_n n_{pe} \exp(qV/kT), \quad (4)$$

where D_n is the electron diffusion constant, τ_n is the lifetime, and n_{pe} is the equilibrium electron concentration at the edge of the junction on the p side. Since the reciprocal of the lifetime is proportional to the concentration of defects which act as recombination centers,

$$1/\tau_n = (1/\tau_0) + K\Phi \text{ sec}^{-1}, \quad (5)$$

where K is the damage constant and Φ is the γ fluence. Combining Eqs. (4) and (5), one obtains the following for the intensity at a constant voltage¹⁰:

$$(I_0/I) - 1 = \tau_0 K \Phi, \quad (6)$$

where I_0 is the light intensity before irradiation. In deriving this equation we have employed another experimental result. That is, the maximum concentration of defects achieved in this study is far too low to affect the majority carrier concentrations in either the n - or p -type regions. Consequently, n_{pe} is a constant. To test Eq. (6) and further confirm the existence of diffusion-controlled light emission at 300 °K, a laser diode was irradiated at 300 °K and measured at constant voltage at intervals during the irradiation. The results are shown on the log-log plot in Fig. 3, where $(I_0/I) - 1$ is plotted versus Φ . The straight line drawn through the points has a slope of one, indicating the validity of Eq. (6). According to the curve, $\tau_0 K$ is $1.7 \times 10^{-17} \text{ cm}^2$. If τ_0 is assumed to be about 10^{-9} sec , then K is $1.7 \times 10^{-8} \text{ cm}^2/\text{sec}$, which is typical of the damage constants for γ -irradiated Si.²³ In conjunction with the observation that I is proportional to $e^{qV/kT}$, the agreement between the data and Eq. (6) tends to support the idea that the light emission is diffusion controlled at 300 °K. Consequently, changes in light intensity at 300 °K with irradiation essentially reflect

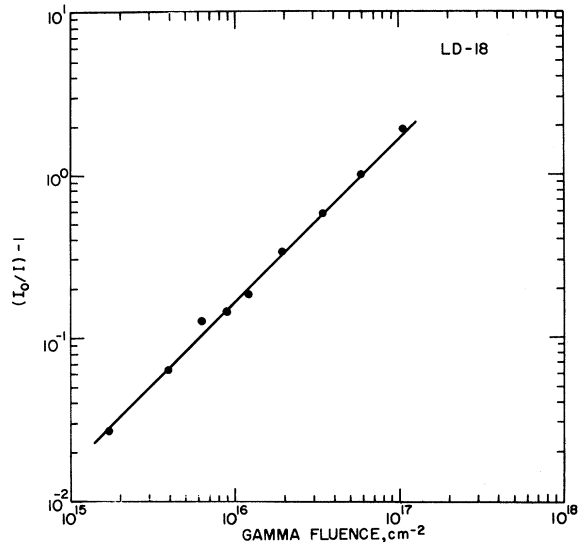


FIG. 3. Degradation of light intensity, as measured at constant voltage, versus Co^{60} γ -ray fluence. Irradiation temperature: 300 °K.

a decrease in lifetime due to the introduction of nonradiative recombination centers.

It is important to point out that the effect of these irradiations on the total current in the diodes is negligible. The J - V characteristics shown in Fig. 1 do not change significantly following irradiation.

Thermal Annealing

It is desirable to present thermal- and injection-annealing results in the form of unannealed fractions. For measurements at 300 °K, we wish to compute f , the unannealed fraction, on the basis of a change in lifetime and not merely as a fractional change in light intensity. For constant voltage measurements, the computation is the same for I or τ_n , since I is proportional to τ_n . However, measurements carried out in the pulse mode were constant-current measurements. For recombination within the space-charge region, the current density takes the form²⁴

$$J \approx \text{const} \times (1/\tau_n) e^{qV/2kT}. \quad (7)$$

Solving for $e^{qV/2kT}$, and substituting in Eq. (4) reveals that I is proportional to τ_n^3 at constant current. In this case, we can define and compute f as follows:

$$f = \frac{(1/\tau_f) - (1/\tau_0)}{(1/\tau_f) - (1/\tau_0)} = \frac{(1/I_f)^{1/3} - (1/I_0)^{1/3}}{(1/I_f)^{1/3} - (1/I_0)^{1/3}}, \quad (8)$$

where τ_f and I_f correspond to the values obtained immediately after irradiation.

The results of isochronal-annealing measurements are illustrated in Fig. 4, in which the un-

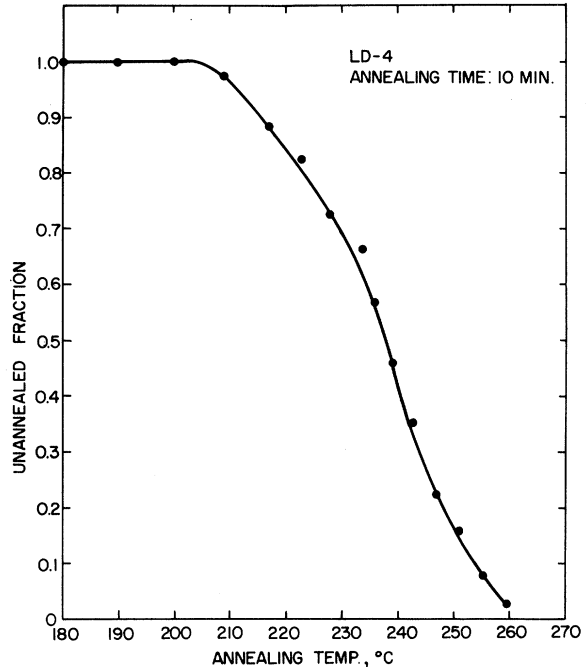


FIG. 4. Isochronal annealing characteristics of a typical Co^{60} -irradiated laser diode.

annealed fraction, computed from Eq. (8), is plotted versus annealing temperature. The intensity values used to calculate f were obtained by measuring the light emission at 300 °K following each anneal. No annealing occurred below 200 °C. Complete recovery occurred in a single annealing stage centered at about 237 °C for annealing times of 10 min.

The results shown in Fig. 4 differ somewhat from those seen in p -type GaAs by other investigators. Aukerman and Graft²⁵ observed three annealing stages centered at 155, 240, and 350 °C in the recovery of conductivity in electron-irradiated boat-grown material. The fact that the 155 and 350 °C stages are not observed in this study can probably be attributed to differences in the type of material or in the type of measurement. Arnold¹ also observed the low-temperature stage in the luminescence recovery of electron-irradiated boat-grown p -type GaAs. However, only the emission band at 1.37 eV recovered at this temperature. Recovery of the near-edge emission at 1.47 eV occurred at 240 °C in agreement with our results. Since the 1.37-eV band is usually not observed in epitaxial material,¹ the absence of the 155 °C stage in this study is attributed to material differences. Tkachev *et al.*⁴ and Hwang²⁶ have suggested that the 1.37-eV band is associated with arsenic vacancies, while Arnold¹ has associated changes in the lattice coupling of

the 1.37-eV band at 155 °C with the motion of gallium vacancies. In either case, one might expect to see a growth of this band with irradiation as observed by Tkachev *et al.*⁴ Apparently, in our case the effect of the luminescence "killer" center which anneals at 240 °C overwhelms any other weaker luminescence band which grows with irradiation and annealing below 240 °C. The fact that the 1.37-eV band is not observed after annealing to 240 °C is in conflict with observations by Tkachev *et al.*⁴

The isochronal-annealing stage shown in Fig. 4 is relatively sharp, suggesting the possibility that the kinetics of thermal annealing may be simple. This possibility provided the motivation for carrying out isothermal-annealing experiments in which defect annealing is measured as a function of time at a given temperature. Figure 5 illustrates the results of these measurements for a few of the temperatures at which isothermal-annealing curves were obtained. Since complete recovery could be achieved by annealing at 275 °C, the same diode was used for all the isothermal-annealing runs, as well as the isochronal-annealing curve shown in Fig. 4. The minimum annealing time used in obtaining the data in Fig. 5 was much longer than the time required to establish thermal equilibrium in the furnace. The series of curves in Fig. 5 demonstrates that f varies exponentially with time:

$$f = e^{-\lambda t}, \quad (9)$$

where λ is a temperature-dependent rate constant of the form

$$\lambda = \lambda_0 e^{-E_A/kT} \text{ sec}^{-1}. \quad (10)$$

The preexponential factor λ_0 is the frequency at which the defects approach a potential barrier of height E_A . Equation (9) indicates that the defects

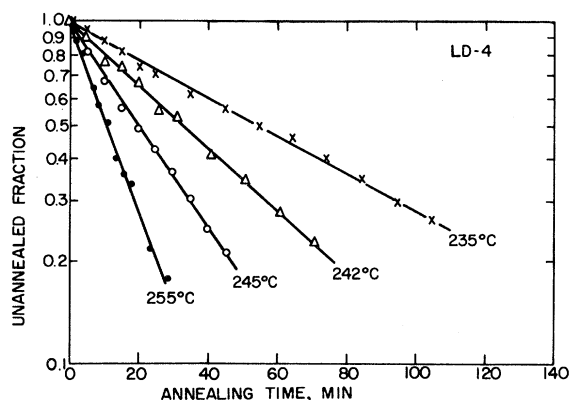


FIG. 5. Isothermal-annealing curves obtained at various temperatures for a Co^{60} -irradiated laser diode.

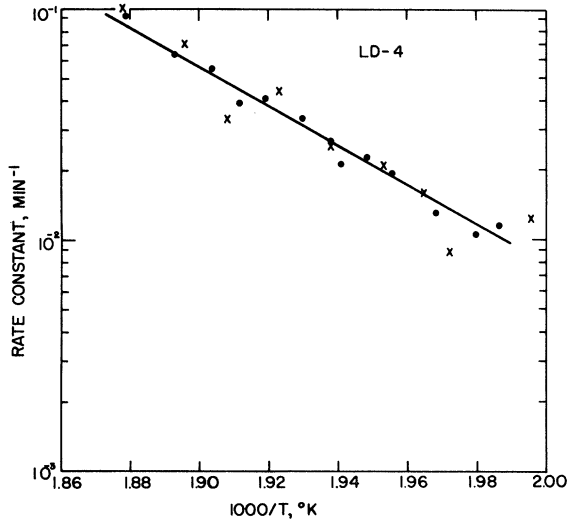


FIG. 6. Rate constants determined from isothermal-annealing curves versus reciprocal temperature. The x symbols represent points derived from an analysis of the isochronal-annealing curve.

anneal by a single first-order process. To find λ_0 and E_A , λ is obtained from the slopes of the curves in Fig. 5 and plotted versus reciprocal temperature as shown in Fig. 6 by the solid circles. As a check on these data, the isochronal-annealing curve (Fig. 4) was analyzed to obtain λ as a function of temperature by integrating the rate equation for a first-order process over the constant time interval used in the isochronal measurements. For the i th anneal,

$$\lambda(T_i) = (1/10 \text{ min}) \ln(f_{i-1}/f_i) \text{ sec}^{-1}. \quad (11)$$

Knowing T_i and the f values before and after the i th anneal, $\lambda(T_i)$ can be calculated. The x 's in Fig. 6 were computed in this way and tend to agree with the rate constants obtained from isothermal annealing. The straight line drawn through the experimental points gives $E_A = 1.70 \pm 0.05$ eV and $\lambda_0 = 1.2 \pm 0.2 \times 10^{13} \text{ sec}^{-1}$. Aukerman and Graft²⁵ have also observed first-order annealing processes above 200 °C in both n - and p -type GaAs. For the 240 °C stage in p -type material, they obtained $E_A = 1.3$ eV, somewhat smaller than our value of E_A .

Forward-Bias Annealing

Although these defects are thermally stable at 300 °K, they can be easily removed at this temperature by forward biasing the diode. In fact, measurements cannot be made on irradiated diodes using a dc forward current greater than 10 A/cm^2 without producing some annealing after a few measurements. The same is true of pulsed measure-

ments at higher currents. As indicated in an earlier section, the diodes were run at an applied voltage of 5 V using 180-nsec-wide pulses at 90Hz. Under these conditions, a larger applied voltage would cause some annealing within $\frac{1}{2}$ h. Consequently, it was necessary to run the diodes at relatively low currents. This precluded studying the damage by measuring the diodes at 300 °K under lasing conditions.

As stated earlier, the application of heavy forward bias occasionally degraded unirradiated diodes. However, if the diodes were forward biased below this degradation level at 300 °K, they could be returned to their preirradiation output levels, indicating that all the damage can be removed by applying a forward bias. In all cases, the forward-bias annealing was accomplished following irradiation. For comparison, one diode was forward biased during irradiation, and the same fraction of defects remained as if an equal forward bias had been applied following irradiation. With regard to this result, it is important to note that the excess minority carrier density generated by the γ -irradiation facility is far too low to cause any bias annealing. The excess density generated is approximately $g\tau_n$ where g is the generation rate of electron-hole pairs caused by the GIF. For the irradiation position used in these experiments, g is about $10^{16} \text{ cm}^{-3} \text{ sec}^{-1}$. Using $\tau_n = 10^{-9} \text{ sec}$, we see that $g\tau_n \approx 10^7 \text{ cm}^{-3}$, a value much lower than that resulting from heavy forward bias.

The recovery in the light output at 300 °K re-

sulting from the application of high-current pulses at various temperatures is shown in Fig. 7. Each point corresponds to one 3- μsec -wide pulse applied across the diode and a 100- Ω series resistor. At room temperature the forward-bias annealing proceeds readily. As the temperature is lowered, the amount of recovery decreases for a given pulse size. Below 100 °K no recovery is observed in these measurements in agreement with Compton and Cesena's¹³ results. However, dc forward-bias annealing reveals that recovery can be achieved at 76 °K. The experimental results indicate that the degree of recovery obtained by forward biasing at low temperatures depends on the temperature at which the light emission is observed. To illustrate this fact, a diode was irradiated and then measured at 76 and 300 °K. After irradiation the light intensity was reduced to the point where $I/I_0 = 0.35$ as measured at 300 °K, and $I/I_0 = 0.55$ as measured at 76 °K. The difference in these two values indicates that the damage constant is smaller for degradation of the light output at 76 °K. Following irradiation, the diode was forward biased at 76 °K for 30 min at $2.2 \times 10^2 \text{ A/cm}^2$ and then remeasured. The recovery achieved at 76 and 300 °K was $I/I_0 (300^\circ\text{K}) = 0.46$ and $I/I_0 (76^\circ\text{K}) = 0.93$. Consequently, forward biasing at 76 °K produces only a small recovery in the light output at 300 °K but almost complete recovery in the light output at 76 °K. In contrast with this, if a diode is biased at 300 °K for 30 min at $2.2 \times 10^2 \text{ A/cm}^2$, nearly complete recovery is

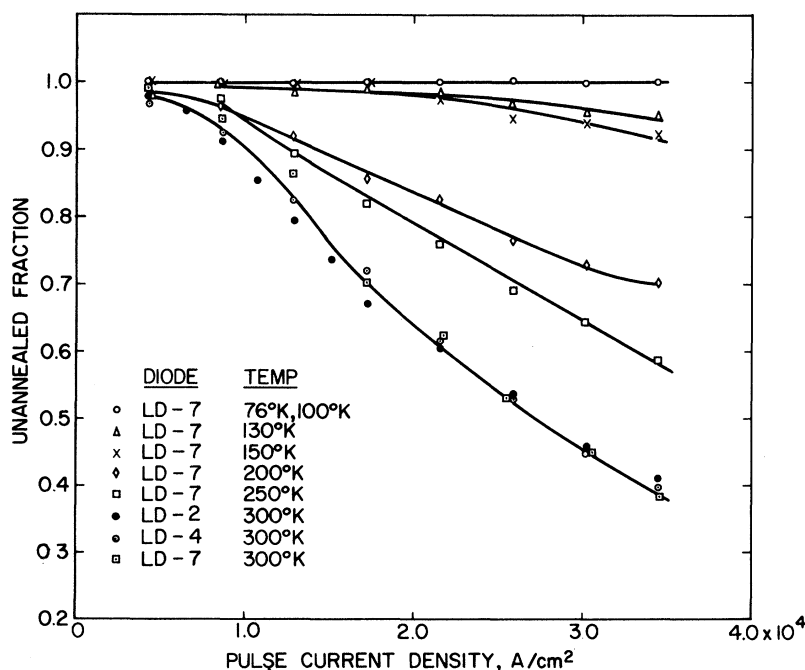


FIG. 7. Forward-bias annealing as a function of diode current density for various temperatures. Each point corresponds to the application of one 3- μsec -wide pulse across the diode at the specified temperature.

observed at both 300 and 76 °K.

To explain the results outlined in the previous paragraph, it is suggested that forward-bias annealing occurs through the capture of injected minority carriers by the defects. For this model, which we will refer to as the injection-annealing model, the defect has a much smaller activation energy E_A in the new charge state resulting from minority-carrier capture, and annealing can take place at a lower temperature. This type of mechanism is known to cause vacancy annealing in p -type silicon at low temperatures.²⁷ The annealing rate will depend on the rate at which the defects capture minority carriers which, in turn, is proportional to Δn_p . Under forward bias, Δn_p at a distance x away from the edge of the depletion layer in the p -type region is given by

$$\Delta n_p = \Delta n_{p0} e^{-x/L_n}, \quad (12)$$

for $\Delta n_p < p$, the hole concentration, where Δn_{p0} is the concentration at $x=0$ for a given voltage and L_n is the electron diffusion length. Consequently, the injection-annealing rate will vary with distance in the p region and will depend on the diffusion length and the forward-bias voltage. Because of the exponential dependence on distance, the amount of annealing that will occur more than a diffusion length away from the junction will be relatively small. If L_n at 76 °K is smaller than L_n at 300 °K, then one would expect to achieve only partial recovery in the 300 °K light emission by forward biasing at 76 °K because the defects located beyond L_n (76 °K) will not be significantly affected. Hence, the region between $x=L_n$ (76 °K) and $x=L_n$ (300 °K) which can contribute significantly to the light emission at 300 °K will still be characteristic of irradiated material. It also follows from this argument that nearly complete recovery should be observed in the 76 °K light emission and that forward biasing at 300 °K should result in nearly complete recovery at both temperatures in agreement with the experimental results.

Two other experimental observations are crucial to the validity of the above explanation. First, the depletion layer width W decreases with decreasing temperature. At 300 °K, W is 0.15 μ at zero bias while, at 76 °K, W is 0.10 μ . This means that the $x=0$ point moves effectively to negative values as the diode is cooled, making it even more difficult to achieve annealing in the region near L_n (300 °K). Secondly, we have assumed that L_n (76 °K) is less than L_n (300 °K). This assumption was verified experimentally by measuring the junction capacitance C_J and the short circuit current I_{SC} generated by a GaAs-filtered constant light source, as a function of reverse bias. In this method one assumes that

$$I_{SC} = a(W+L) A, \quad (13)$$

where $L = L_n + L_p$. Using the fact that $C_J = A\epsilon\epsilon_0/W$, one plots $1/C_J$ versus I_{SC} to obtain L from the intercept

$$1/C_J = -L/A\epsilon\epsilon_0 + (1/aA\epsilon\epsilon_0)I_{SC} F^{-1}. \quad (14)$$

The results are shown in Fig. 8. The deviation from the straight line in the 300 °K case at higher I_{SC} and, hence, larger reverse voltages is usually observed. It indicates the onset of avalanche multiplication resulting in more current than one would predict from Eq. (14). The values for L are L (76 °K) \approx 0.3 μ , L (300 °K) \approx 0.5 μ . Since L_p is usually much smaller than L_n in GaAs,²⁸ these values are approximately equal to L_n . The value of 0.5 μ at 300 °K agrees with the recent determination of Rao-Sahib and Wittry²⁹ of $L_n = 0.6 \mu$ in heavily doped ($3.76 \times 10^{19} \text{ cm}^{-3}$) p -type GaAs.

In the injection-annealing model, the rate of annealing is proportional to Δn_p , implying that the important parameter in bias annealing is the current level and not the total charge transported across the junction during the time the bias is on. This can be verified experimentally by calculating the (JtA) product necessary to produce a given amount of recovery for various types of bias annealing. Here, J is the current density, A is the area, and t is the required bias time, so that JtA equals the total charge transported. For an unannealed fraction of 0.5, the following (JtA) products are obtained for the various types of forward bias at 300 °K: 22 A/cm² dc, $(JtA) \approx 11 \text{ C}$; 87 A/cm² dc, $(JtA) \approx 5 \text{ C}$; and, for a high current pulse of approximately $2.6 \times 10^4 \text{ A/cm}^2$, $(JtA) \approx 5 \times 10^{-5} \text{ C}$. In agreement with the injection-annealing model, we see from these values that the recovery de-

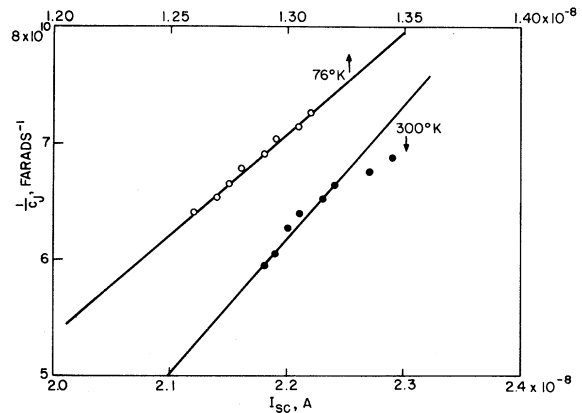


FIG. 8. Reciprocal capacitance versus short circuit current for unirradiated laser diodes at 76 and 300 °K. Reverse-bias voltage range: 0 to 1.0 V.

pendes primarily on the current level and not the total charge, and that the annealing per unit time increases markedly as the current level is increased.

We now wish to use the injection-annealing model to predict the way in which bias annealing proceeds with time and compare this with the experimental results. On the basis of the model, one might expect that the density of defects near the junction will decrease due to injection annealing, but the density approximately a diffusion length away from the junction may actually increase due to the migration of defects into this region. This would mean that the apparent annealing rate would decrease with time due to the increase in defect density away from the junction.

In addition to the possible change in the distribution of defects with distance away from the junction, the annealing rate will be affected by the manner in which the injection annealing proceeds with time. We have shown that the bias annealing depends crucially on the value of Δn_p in accordance with the injection-annealing model. Consequently to facilitate the explanation, we can pick a threshold value Δn_{pt} , above which annealing will be nearly complete in a reasonable time and below which only a small amount of annealing will occur in the same length of time. Here we are defining a reasonable length of time qualitatively and relative to the times involved in doing the measurements, i.e., say, 2 h. Assuming that the contribution to the light emission beyond a diffusion length is relatively small, complete recovery can only be achieved if the forward bias is such that Δn_p at $x = L_{n0}$, the diffusion length in an unirradiated diode, is equal to Δn_{pt} . If the forward bias is lower than this, then $\Delta n_p(x = L_{n0})$ will be less than Δn_{pt} in an irradiated diode and even smaller still in an unirradiated diode, according to Eq. (12), since the value of L_n at $x = L_{n0}$ will be less than L_{n0} . After a reasonably short time, annealing will be complete out to that value of x for which $\Delta n_p = \Delta n_{pt}$ at the particular bias current being used. Beyond this value of x , which we can call x_0 , L_n will be approximately equal to the value of L_n after irradiation. Consequently, Δn_p between x_0 and $x = L_{n0}$ will decrease more rapidly than Δn_p would if the diode were unirradiated. The result is that recovery in this outer region ($x_0 < x < L_{n0}$) becomes very difficult because Δn_p is less than Δn_{pt} throughout the region. In the actual case, some annealing will occur at $\Delta n_p < \Delta n_{pt}$, but it will be relatively slow and may appear to approach a limiting value of recovery. According to the above argument, x_0 will increase toward L_{n0} as the bias current is increased. Consequently, the limiting value of recovery will increase with in-

crease in current.

The experimental results of bias annealing as a function of bias time are shown in Fig. 9 for both 76 and 300 °K. In all three cases, the bias annealing and the light-output measurement were done at the same temperature. The shape of these curves is similar to that observed for forward-bias annealing of both neutron and γ -ray damage in Si.^{30,31} In agreement with predictions based on the injection-annealing model, there is a very rapid recovery initially, and then the rate of annealing decreases considerably and approaches a limiting value. Also in agreement with the explanation presented above, the limiting value occurs at a larger value of recovery (smaller value of f) as the bias current is increased.

It is important to point out that the different injection mechanisms (tunneling) which may prevail at 76 °K do not invalidate the injection-annealing model. Regardless of the injection mechanism, the minority-carrier density will decrease with distance into the p region as $\exp(-x/L_n)$. One would also expect the injection-annealing model to hold if radiative recombination occurs in the depletion layer at 76 °K. As in the diffusion-controlled case, the electrons present at 76 °K could not reach the 300 °K light-emission region. How-

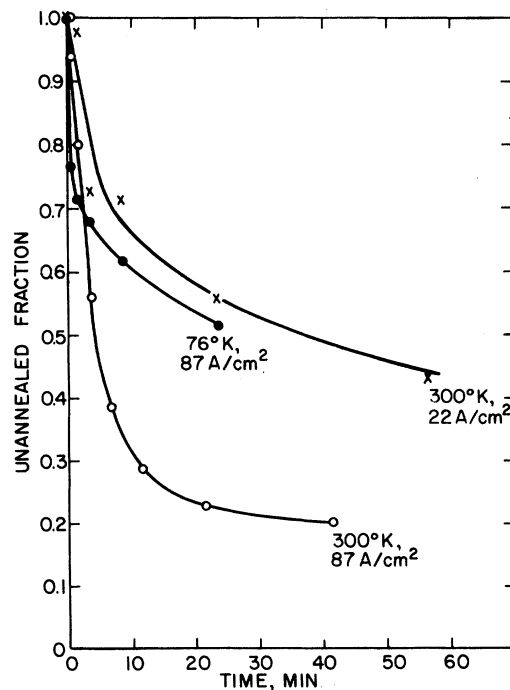


FIG. 9. Recovery due to forward bias versus time that the bias was applied. For each curve the bias and the light-emission measurement were both done at the indicated temperature.

ever, annealing of the 76 °K light emission would occur readily since the ratio of electron density to hole density in the depletion layer will be even higher than it is in the neutral p region.

Another point which must be considered is the possibility that heating during application of the bias is responsible for the bias annealing. We feel that this is a negligible effect in our case for the following reasons. First, the diode would have to be heated up to 210 °C before any significant annealing would be observed. For pulse operation Nelson *et al.*³² estimated that, at a current density of 10^5 A/cm², the temperature rise would be 60 °C for each microsecond of pulse width. Although the pulses used in forward-bias annealing were 3 μ sec wide, the largest current density used was about 3×10^4 A/cm². Therefore, it does not appear that a temperature greater than 200 °C was achieved during pulsing. Second, in the case of dc bias annealing, the forward bias was applied for much longer time periods but the current density was much smaller. When bias annealing was done with a curve tracer, the J - V characteristic could be monitored during annealing. No significant change was ever observed in the J - V curve during an anneal. However, if hot air was blown on the diode during the anneal so that the diode temperature rose to approximately 80 °C, the J - V curve would shift significantly due to the external heating. For dc bias at 76 °K, the chance of heating is even more remote because the diode was in direct contact with liquid nitrogen.

Spectral Measurements

Measurements of the emission spectrum were carried out at 76 °K to ascertain the effect of irradiation on the spectrum. In unirradiated diodes operated below the laser threshold, the most intense band is the near-edge emission at 1.47 eV which results in lasing at higher currents. An emission band at 1.37 eV was observed occasionally, but it was very weak. This agrees with previous observations¹ which indicate that this band while very strong in bulk-grown material is usually absent from epitaxial GaAs. Weak long-wavelength bands were also observed at 1.28 and 0.97 eV in agreement with previous measurements by Millea and Aukerman.⁹ None of the long-wavelength bands appear to grow with irradiation or annealing. In addition, the lasing emission band does not exhibit a wavelength shift greater than the resolution of the small monochromator following irradiation or annealing. The shape of the emission spectrum at 300 °K is also independent of irradiation. This is important because the emission at 300 °K occurs in a wavelength region where the response of the 7102 photomultiplier is decreasing

with increasing wavelength. Consequently, any wavelength shift in the emission band to longer wavelengths with irradiation would have distorted the results obtained without a monochromator at 300 °K.

DEFECT MODEL

The proposal of a detailed defect model in a relatively unexplored material like GaAs is a somewhat speculative procedure. However, it is informative to consider what type of model satisfies the experimental results and the results of previous investigations. In doing so, it is difficult to ignore the history of defect modeling in semiconductors. In both Si and Ge, early work³³ suggested that isolated native defects were stable at room temperature. However, this has been proven false, and it is now commonly accepted that vacancies and interstitials can move at very low temperatures in Ge and Si. With this in mind, one is reluctant to suggest that an isolated native defect in GaAs is stable at 200 °C. In fact, there is ample evidence that defect motion occurs below room temperature in compound semiconductors. Vook^{34,35} has shown that defect motion occurs in InSb, GaAs, and CdS at temperatures as low as 50 °K. Stein³⁶ has observed carrier concentration recovery in electron-irradiated epitaxial n -type GaAs below 300 °K. Potts and Pearson³⁷ also observed extensive annealing at room temperature in quenched samples of n -type GaAs. In addition, Gobeli and Arnold³⁸ attributed luminescence degradation in electron-irradiated GaAs to the migration and trapping of As defects at luminescence centers. Further difficulty is encountered with the identification of the defect as an As vacancy, if one compares our results with those of Arnold.¹ Through quenching experiments, Potts and Pearson³⁷ established that the annealing observed at 220 °C in n -type GaAs was due to the motion of an arsenic vacancy-associated defect. Arnold drew an analogy with this and suggested that the recovery of luminescence at 240 °C in p -type GaAs was due to the annealing of As vacancies which act as killer centers. However, if this is the case, then our injection annealing model suggests that the As vacancy should anneal at room temperature in n -type material, which does not agree with the conclusions of Potts and Pearson.

It is tempting to identify the defect responsible for the 240 °C stage in our study with one of the annealing stages observed by Aukerman and Graft²⁵ in electron-irradiated n -type GaAs. They found that part of the annealing occurring at 220 °C could be characterized by a first-order process with $E_A = 1.55$ eV and $\lambda_0 \approx 10^{13}$ sec⁻¹. In addition to the similarity between values for E_A and λ_0 in their

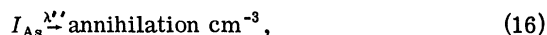
case and ours, Aukerman and Graft observed that this annealing stage proceeded more rapidly for higher electron concentrations in agreement with our forward-bias annealing results. However, there are two major difficulties associated with equating the defects in both cases. First, Aukerman and Graft's results indicate that the rate constant would be extremely small in *p*-type GaAs, precluding any annealing at a similar temperature such as 240 °C. Aukerman and Graft suggested that this problem could be resolved if a different annealing mechanism prevailed in *p*-type GaAs. However, the second difficulty makes the identification even more remote. If the defects are the same, then our injection-annealing results indicate that the defect should not be stable at 300 °K in the presence of a significant electron concentration ($\sim 10^{16} \text{ cm}^{-3}$) as in the case of the *n*-type material studied by Aukerman and Graft.

The kinetics of thermal annealing can provide hints as to the nature of the defect which is annealing. A first-order process is characteristic of only certain types of annealing mechanisms. Aukerman and Graft²⁵ suggested that the annealing stage in *n*-type GaAs discussed in the previous paragraph was due to close interstitial-vacancy pair recombination. However, as suggested by Arnold,¹ the results of Vook³⁴ and Potts and Pearson³⁷ make this assignment questionable because their work implies that a close pair is not stable at elevated temperatures. Migration of defects to traps whose concentration is large enough not to be significantly altered by the annealing process can also be a first-order process. A prominent example is the formation of *A* centers in silicon.³⁹ For this type of process the defect takes many jumps to reach the trap and the preexponential factor λ_0 is usually quite small, of the order of 10^6 to 10^8 sec^{-1} .³¹ However, λ_0 in our case is approximately 10^{13} sec^{-1} , of the same order as the maximum lattice-vibration frequency. Consequently, this annealing mechanism does not seem to apply to our case.

We have suggested that an isolated native defect is not responsible for the 240 °C stage observed in this study. An obvious alternative is a complex, such as the *A* center, involving an impurity and a native defect. The results of Vook³⁴ and Potts and Pearson³⁷ suggest that the broad annealing observed below room temperature may be associated in part with the agglomeration of defects and the formation of complexes. In addition, the value of E_A we observe (1.7 eV) is quite a bit larger than typical values for isolated defects.³³ Consequently, we suggest that the defect which anneals at 240 °C is a complex made up of an impurity bound to either an As vacancy or an As interstitial. In order to

decide between the vacancy and the interstitial, recall that under bias the defects annealed at temperatures as low as 76 °K. This fact suggests that the native defect involved is the As interstitial.

One can now ask if the observed kinetics can be accommodated by such a defect. Let us assume that the following reactions take place during annealing:



where N_C is the concentration of complexes and I_0 is a constant impurity concentration. Solving the rate equations for these reactions, one obtains two rate constants, λ_+ and λ_- which govern the exponential variation of N_C and I_{As} with time. However, if one assumes that the rate-limiting step is the breakup of the complex and that once this takes place the I_{As} will annihilate very rapidly, then

$$\lambda'' \gg \lambda' I_0 \text{ sec}^{-1} \quad (17)$$

and $\lambda'' \gg \lambda \text{ sec}^{-1}$,

and the solution reduces to

$$N_C(t) \approx N_{C0} e^{-\lambda t} \text{ cm}^{-3}, \quad (18)$$

with λ given by Eq. (10). This result corresponds with the experimental observations. In addition, one would not expect a value of λ_0 which is characteristic of a migration process since λ_0 is determined by the dissociation of the complex. This also agrees with the experimental results.

To summarize, we have suggested that the defect which thermally anneals at 240 °C and injection anneals at lower temperatures is a complex made up of an impurity and an As interstitial. It is important to note that we have not specified that the complex is necessarily the luminescence killer center. In agreement with Arnold,¹ the killer center could be the As vacancy, and luminescence recovery could occur when the interstitial that is released from the complex migrates to the As vacancy and the pair annihilates. Such alternative models serve to emphasize the fact that the situation is quite complex, and that one can propose defect models only on a tentative basis.

FURTHER IMPLICATIONS

There are two other aspects of the experimental results which should be mentioned. First, the relationship of the results to the gradual degradation of laser diodes which occurs after long operating times. This effect has been observed by several investigators⁴⁰⁻⁴³ and has been explained in several ways. One of the explanations recently used by

Kressel and Byer⁴⁰ is that Frenkel defects are created under lasing conditions. Kressel and Byer found many similarities between the gradual degradation and the effects of electron irradiation. One would expect several types of defects to be created during irradiation of a complex material like GaAs. We can only point out that the defect observed in this experiment is probably not responsible for the gradual degradation observed at 300 °K, since it would not be stable under the heavy injection conditions present during lasing.

The second pertinent point concerns the practical implications of the results obtained herein. If one wishes to operate GaAs laser diodes in a radiation environment at temperatures below 200 °C, then it is a very desirable advantage to be able to eliminate a significant fraction of the defects at temperatures between 76 and 300 °K. As in this experiment, this can be done by changing the mode of operation of the diodes, or, if the laser threshold is high enough, by merely operating the diodes under lasing conditions.

CONCLUSIONS

The light emission at 300 °K below a current density of 2.2×10^2 A/cm² in the type of laser diodes examined in this study is due to diffusion and recombination of electrons in the *p*-type region of the device. For this reason, the Co⁶⁰-induced degradation of the light output at 300 °K is essential-

ly due to a decrease in lifetime resulting from the introduction of nonradiative recombination centers. The defects thermally anneal in a single stage centered at 237 °C. Isothermal-annealing results indicate that annealing occurs by a first-order kinetic process with an activation energy of 1.7 eV. Luminescence recovery can be achieved at temperatures as low as 76 °K by heavily forward biasing the diode. The forward-bias annealing is thought to be due to an increase in the probability of annihilation because of a change in charge state of the defect following capture of a minority carrier. The various aspects of forward-bias annealing observed in this study can be explained by this model. On the basis of the above results, it is postulated that the defect is a complex consisting of an impurity and an As interstitial. However, this identification is highly tentative, and we wish to emphasize again that a great deal more work will be required to positively identify the defects present in a complex material like GaAs.

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Electronic Band Structure and Optical Properties of Graphite from a Variational Approach*

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The electronic band structure of graphite has been calculated from an *ab initio* variational approach using a linear-combination of atomic-orbitals (LCAO) basis of Bloch states, including nonspherical terms in the one-electron crystal potential. Matrix elements of the Hamiltonian are evaluated directly without any tight-binding approximations. The optical transitions deduced from the energy bands calculated using a single-layer crystal model agree nicely with recent polarized-light reflectance measurements. Details of the band structure are calculated for the three-dimensional Brillouin zone and related to the results obtained using the single-layer crystal structure. The results are encouraging, not only from the standpoint that the method employed is an *ab initio* approach with no special *a priori* assumptions, but also because the band structure is quite insensitive to the particulars of the crystal potential function.

I. INTRODUCTION

There has been much interest recently in the properties of crystals exhibiting strongly anisotropic behavior: Of these, graphite is an excellent example of a substance illustrating the effects of greatly differing bonding in different crystallographic directions. While the carbon atoms in the cleavage planes of graphite are strongly bound among themselves, the adjacent planes are bonded together very weakly.

As a consequence of the large interlayer spacing in graphite, most of the optical characteristics of the substance can be well understood on the basis of a single-layer crystal structure.¹ Reflection in the layer plane σ_h is a symmetry operation for the single layer, and states can be classified accord-

ing to their parity with respect to σ_h . Thus selection rules can be easily determined for transitions with the incident electric field parallel or perpendicular to the c axis. Since the interaction between different planes is small, the breakdown of the selection rules in the three-dimensional Brillouin zone for $k_z \neq n\pi/c$ is such that transitions "forbidden" for the single-layer structure still are not expected to contribute very significantly for the multiple-layer crystal. Thus, optical experiments with polarized light can be quite useful in gaining an understanding of the electronic structure of graphite.

Experimental results on the anisotropy of the optical constants of graphite have recently been determined¹ in the energy range 2–10 eV. As far as the optical properties are concerned, it turns