Luminescence in Intrinsic and Annealed Electron-Irradiated GaAs:Cd†

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The lasing transition in boat-grown cadmium-doped GaAs is similar to that previously found in GaAs:Zn. In cadmium-doped GaAs, the three excited states of this transition (C', B', and A') lie at energies of 1.484, 1.486, and 1.507 eV, respectively. In addition, there is a broad-band emission peak centered at 1.37 eV. All of these peaks move to lower energies with decreasing excitation intensity. 1.5-MeV electron irradiation causes exponential decreases in the broad-band and near-band-edge intensities with increasing electron fluence for fluences greater than 10^{16} e/cm^2. Isochronal annealing of the irradiated material in the temperature range 50–190°C causes increases in the emission centered about 1.37 eV, but the emission is modified and appears as two peaks (Cd 0, and Cd 1) at 1.369 and 1.337 eV. The temperature dependence of the intensity of the peaks indicate that Cd 1 is a phonon replica of Cd 0. The development of the structure is interpreted as occurring when Ga vacancies migrate and form localized modes that weaken the coupling of the Cd 0 defect to the lattice. Diminution of intensity and loss of structure are observed in the temperature range 190–240°C and result from a decrease in the number of centers giving rise to localized modes. The killer center which degrades the luminesence is believed to be the As vacancy which anneals out at about 240°C. The energy shift of the lasing transition and of the broad-band emission are interpreted to indicate that both bands are the emission envelopes of unresolved donor-acceptor pair transitions. The lasing transition arises from the recombination of holes localized at neutral Cd acceptors, with electrons localized at donors, possibly Si; whereas the broad-band emission is due to pair annihilation involving the same donor and Cd in a different charge state.

INTRODUCTION

RADIATIVE recombination in boat-grown GaAs doped with donors or acceptors is characterized by near-band-edge emission with half-widths of the order of kT, and by broad-band emission where the peak intensity may lie between 0.15 and 0.87 eV from the band edge. This emission has widths of 0.1–0.2 eV. Broad-band emission is not usually seen in low-temperature solution-grown material or in material grown by epitaxial methods. Because the spectral position of this type of emission seems to depend on the particular dopant involved, it is assumed that the broad-band emission arises at a center involving the dopant. Since it does not appear in solution-grown or epitaxially grown material, it is further assumed that an intrinsic lattice defect forms a part of the center. It is known that epitaxial growth and solution growth have a relatively low impurity content and also have fewer stoichiometric deficiencies because of the lower crystal formation temperature. Williams[1] has analyzed the broad-band emission near 1.2 eV, which he has observed for the n-type dopants C, Si, Ge, Sn, S, Se, and Te, and has concluded that this emission is similar to the self-activated luminescence in ZnS, i.e., that the center involves a lattice vacancy, in this case Ga, and a nearby donor. The peak shifts in energy with the particular dopant involved.

The p-type dopants, Zn and Cd, have broad-band emission peaks at 1.38 and 1.37 eV, respectively. In the case of GaAs:Zn, experimental procedures involving fast-electron irradiation followed by annealing revealed that the 1.38-eV peak is due to the replication of three sharp no-phonon lines centered about 1.44 eV.[2] It was argued[3] that the lines were due to bound-exciton annihilation at a center involving Zn^- and a nearby lattice defect, probably a vacancy. The near-band-edge emission (lasing transition) in boat-grown GaAs:Zn has been shown[4] to possess structure. Three lines (width ~0.01 eV) are observed at 1.504, 1.489, and 1.484 eV. The temperature dependence of the intensity of these lines indicates that the transition is from three excited states to a ground state with lines A' and B' representing states which become populated at higher temperatures.

The present paper gives results concerning the changes in both near-band-edge and broad-band luminescence of boat-grown cadmium-doped GaAs upon fast-electron (1.5-MeV) irradiation and subsequent thermal annealing. The luminescence degradation, the energy shifts of the emission, and the changes in luminescence after annealing have been interpreted in terms of specific models for the quenching or "killer" center and for the transition mechanism of the luminescent centers. In addition, it is shown that the lasing transition in boat-grown GaAs:Cd possesses structure which closely resembles that found[4] in GaAs:Zn.

EXPERIMENTAL

The samples used were taken from a Cd-doped ingot boat grown by Monsanto Chemical Co. and having a carrier concentration of 2.5×10^{17} holes/cm^3. Sample faces were approximately parallel to the (111) plane. Sample preparation consisted of a bromine-alcohol etch immediately before measurements were made. Optical

† Work supported by the U. S. Atomic Energy Commission.
[1] E. W. Williams, Phys. Rev. 168, 922 (1968).
[2] G. W. Arnold, Phys. Rev. 149, 679 (1966).
[3] G. W. Arnold and D. K. Brice, Phys. Rev. 178, 1399 (1969).
[4] G. W. Arnold and D. K. Brice, Appl. Phys. Letters 13, 51 (1968).

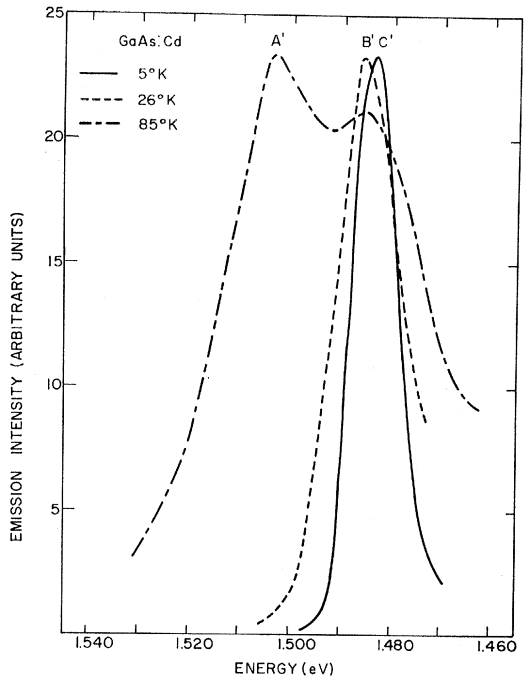

FIG. 1. Near-band-edge luminescence intensity versus energy in GaAs:Cd at 5, 26, and 85°K. Intensities of A', B', and C' have been normalized to the same value.

injection was by means of a 200-W high-pressure mercury arc. After appropriate filtration, the front-surface emitted light was scanned by a Perkin-Elmer 210 monochromator and detected by an RCA 7120 photomultiplier tube.

Annealing experiments were performed in a cold-finger Dewar with heat exchanger in which it was possible to heat the sample block to temperatures as high as 500°C and quench rapidly to temperatures near 25°K. Measurements at temperatures lower than 25°K were made in another Dewar in which the sample could be either immersed in liquid He or in the boil-off gas from a liquid-He reservoir Dewar. For either Dewar set-point temperatures (Chromel-constantan thermocouple) could be maintained within ±0.5°K. Irradiations were made at a sample temperature near 80°K with fast electrons (1.5 MeV) from a 0.5–2.0-MeV Van de Graaff generator.

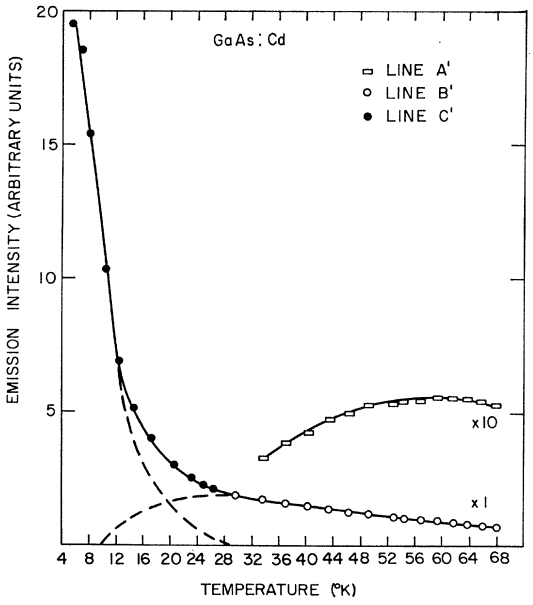

FIG. 2. Emission intensity of lines A', B', and C' versus temperature.

RESULTS

Measurements of luminescence intensity in the 5–90°K temperature range show that the near-band-edge luminescence in GaAs:Cd possesses structure. The observed transitions are shown in Fig. 1, where the intensities have been normalized to the same peak value. The transitions A', B', and C' occur at energies of 1.507, 1.486, and 1.484 eV. The temperature dependence of the transitions is shown in Fig. 2. Lines C' and B' cannot be resolved separately at a given temperature because of their width and small energy separation. The growth of line B' is indicated by a sudden shift in peak energy to higher energies as temperature is increased and by the change in half-width of the composite intensity envelope. The relative amounts of line C' and line B' intensity have been estimated from half-

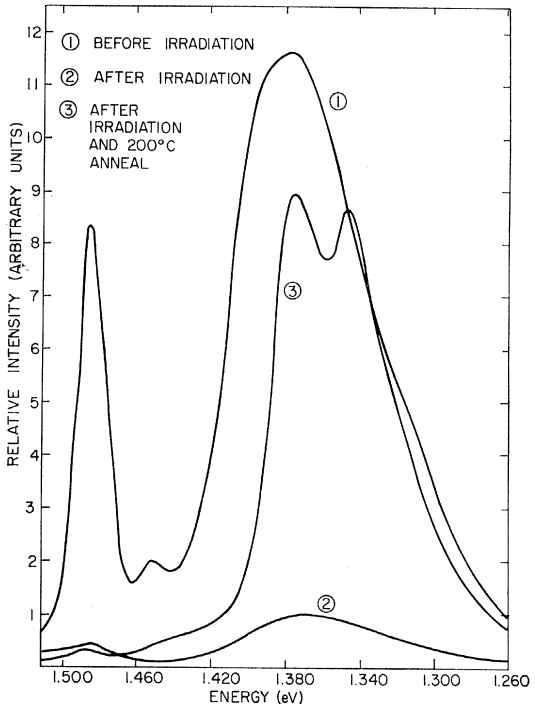

FIG. 3. Near-band-edge and broad-band emission intensity versus photon energy in GaAs:Cd at $T=25$°K, (1) before irradiation, (2) after 5×10^{16}–1.5 MeV e/cm², and (3) after irradiation as in (2) followed by 15-min anneals between 50 and 200°C.

width measurements, and their separate intensities are shown by the dashed curves in Fig. 2.

The results shown in Figs. 1 and 2 are very similar to those obtained[4] in boat-grown GaAs:Zn. In that case, the energies of lines A', B', and C' were at 1.504, 1.489, and 1.484 eV. The temperature dependence of the line intensities was also quite like that shown in Fig. 2. These results clearly indicate that for both p-type dopants, Zn and Cd, in boat-grown GaAs, the lasing transition is from three excited states to a ground state, the higher levels B' and A' being thermally depopulated at lower temperatures.

The luminescent spectra of Cd-doped GaAs at 25°K is shown over a larger energy range in Fig. 3, curve 1. The lasing transition is due to transition B', this state being populated at this temperature at the expense of the ground state. A one-phonon replica of this peak is seen on the low-energy side separated by 0.036 eV, the approximate LO phonon energy for GaAs. The broad-band emission is peaked at 1.37 eV and has a width at half-maximum of about 0.08 eV. These spectra are not corrected for instrument and detector response, but this should not drastically effect the spectral shapes in the region under consideration. Both the B' peak and the broad-band peak move to lower energies as the exciting intensity is decreased. The B' energy shift is about 0.01 eV when the excitation intensity is decreased by a factor of 14, while that of the broad-band peak is about 0.006 eV.

The changes in the broad-band emission as a function of electron fluence are shown in Figs. 3 and 4. The sample was irradiated with 1.5-MeV electrons at 80°K, and measurements were made at about 25°K without intervening warmup. In addition to the degradation of luminescence, there is also a small shift in the peak position toward lower energies. The shape of the emission band does not seem to be appreciably altered. This is in contrast to the behavior of the lasing transition B' which, while also suffering degradation, moves to higher energies with increasing fluence. The change in peak position of this band as a function of fluence is shown in Fig. 5. The peak intensity of both bands is plotted logarithmically against electron fluence in Fig. 6, and the relationship is seen to be exponential after the initial exposure. The intensities of both bands decrease at the same rate. The exponential decay of luminescence with electron irradiation has been noted previously in GaAs and other III-V compounds.[5]

After irradiation to a fluence value of 5×10^{16} e/cm^2, the sample was isochronally (15 min) annealed beginning at 50°C. The resulting changes in the broad-band emission after some of these anneals are shown in Fig. 7. No changes in the spectra were noted until the sample temperature was elevated above room temperature. Changes were noted at temperatures as low as

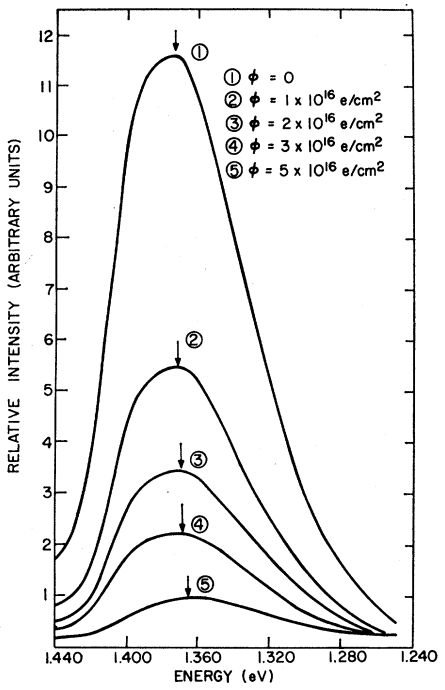

FIG. 4. Broad-band emission intensity versus photon energy for GaAs:Cd for (1) unirradiated material and for 1.5-MeV electron fluences of (2) 1×10^{16} e/cm^2, (3) 2×10^{16} e/cm^2, (4) 3×10^{16} e/cm^2, and (5) 5×10^{16} e/cm^2. $T=25$°K. Arrows indicate maxima of the respective curves.

50°C. No changes in emission were observed for unirradiated GaAs:Cd in the temperature range under discussion. Broad-band emission intensity begins to recover at about 50°C, but the appearance of the band is altered. Two peaks are now observed; the first (Cd 0) is at 1.369 eV, while the second (Cd 1) is as 1.337 eV. The separation, 0.032 eV, is significantly different from the LO phonon energy of 0.036 eV, but the considerable overlap of the two bands is believed to account for the

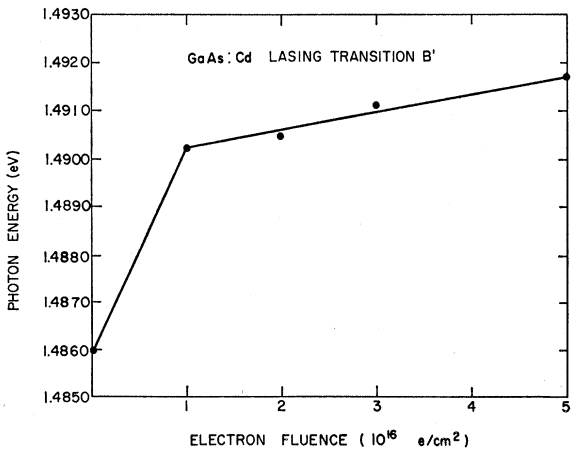

FIG. 5. Energy position of the maximum of the near-band-edge emission peak in GaAs:Cd as a function of 1.5-MeV electron fluence. $T=25$°K.

[5] G. W. Arnold and G. W. Gobeli, in *Radiation Effects in Semiconductors*, edited by F. L. Vook (Plenum Press, Inc., New York, 1968), p. 435.

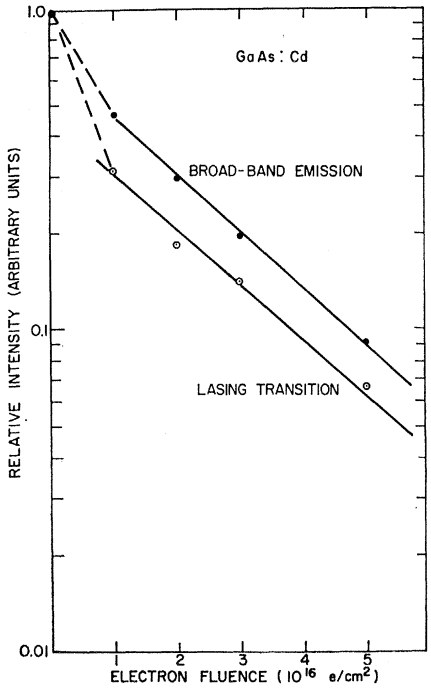

FIG. 6. Relative emission intensity of the 1.48 eV and broad-band emission peaks versus 1.5-MeV electron fluence. $T=25°K$.

difference. If this is the case, then Cd 1 is the first phonon replica of Cd 0. As annealing progresses another replica can be seen on the low-energy side of Cd 1. The relative peak heights remain the same throughout the annealing process and from sample to sample.

The temperature dependences of the intensities of the Cd 0 and Cd 1 lines were measured for a sample in which the annealing process was terminated at 200°C. The results are shown in Fig. 8 for the Cd 0 line which could be followed over a larger temperature range. The intensity of the Cd 1 line changed in the same manner, strengthening the argument that it is a phonon replica of line Cd 1. The binding energy obtained from the slope of the line is about 0.10 eV.

The buildup of emission intensity of the two peaks reaches a maximum near the annealing temperature of 190°C. The near-band-edge emission B' remains relatively unchanged from its value after electron irradiation. Above 190°C there is a rapid diminution of intensity, and the Cd 0 and Cd 1 peaks become poorly resolved. After the 240°C annealing temperature, the broad-band emission intensity and that of the near-band-edge peak begin to increase. Figure 9 shows the two emission peaks before irradiation and after irradiation plus annealing to 280°C. There is still some evidence for the existence of the Cd 0 and Cd 1 lines. In addition, there is now a third shoulder on the high-energy side of the band. Nothing is known about the origin of this peak. The peak of the B' transition has moved back to a position which is lower in energy than before irradiation.

DISCUSSION

Luminescence Degradation Models

The data of Fig. 6 show an exponential decrease of the intensity for both the B' lasing transition and the broad-band emission with electron fluence after an initial nonexponential decrease for fluences below 10^{16} e/cm^2. Rosenstock and Schulman[6] have studied luminescence degradation in terms of two distinct models. One of these models postulates the formation of a killer center volume created by a single radiation damage event in which all luminescence from centers inside the volume is quenched. They have shown that for low levels of radiation, where such killer centers would be widely dispersed, the intensity decreases linearly with the damaging fluence. At higher levels where overlap of the volumes occurs, the relationship becomes exponential.

A second possible model is that in which a transfer of energy is made from the position of the initial radiation damage site to a distant site at which the energy is deposited, and luminescence at that site is quenched. This would be the situation, e.g., in which an exciton is created and travels through the crystal to either a damaged center or a center which can luminesce upon receiving the exciton energy, or, e.g., in which a dis-

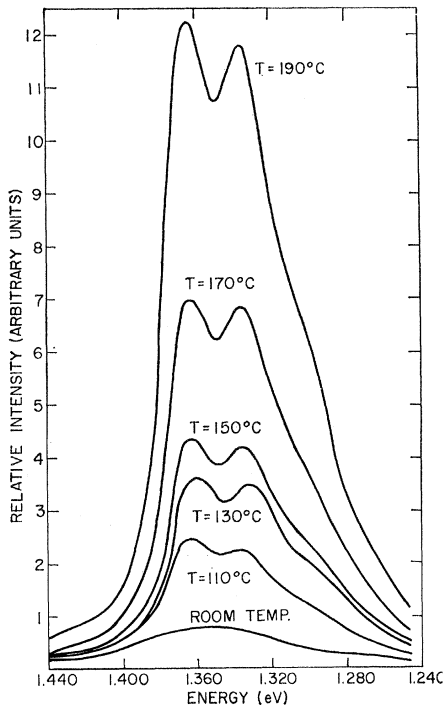

FIG. 7. Relative broad-band emission intensity versus photon energy in GaAs:Cd after irradiation with 5×10^{16}–1.5 MeV e/cm^2 at 85°K and 15-min anneals at the indicated temperature. Measurements made at 25°K.

[6] H. B. Rosenstock and J. H. Schulman, in *Localized Excitations in Solids*, edited by R. F. Wallis (Plenum Press, Inc., New York, 1968), p. 330.

placed atom migrates until a luminescing center is reached. Rosenstock and Schulman have solved this random-walk problem and have shown that at low fluences the degradation will be linear with fluence Φ and will decrease as $1/(1+\varphi)$ at higher fluences.

The degradation of luminescence shown in Fig. 6 clearly does not follow a $1/(1+\varphi)$ law at high electron fluences. The killer center volume concept is, therefore, tentatively adopted in GaAs:Cd, not only because it predicts the form of the luminescence degradation, but because, as shown below, it allows reasonable interpretations of the energy shifts of the emission for donor-acceptor pair transitions as the specific recombination mechanism.

It is possible to obtain some measure of the size of the proposed killer center volumes. If it is assumed in Fig. 6 that a value of 1×10^{16} e/cm^2 represents a limiting fluence, for which the killer center volumes have just begun to overlap, the killer center radius is given, on the average, by $R_k\leq(3/4\pi N)^{1/3}$, where N is the number of atoms displaced by the 1×10^{16} e/cm^2 fluence at an energy of 1.5 MeV. For a lattice displacement threshold energy of 20 eV, $N=1.54\times10^{18}/cm^3$ for which $R_k\leq250$ Å. The luminescence of both emission bands degrades, as shown in Fig. 6, by roughly a factor of 2 at a fluence of 1×10^{16} e/cm^2. The number of displaced atoms is less than the number of Cd acceptors by an order of magnitude. Therefore, assuming the Cd acceptor level is involved in the emission of both bands, each killer center volume quenches about five luminescent centers. If the average volume occupied by an acceptor has a radius R_A then $R_A\cong5^{1/3}R_A$. For 2.3×10^{17} acceptors/cm^3, R_A is the order of 100 Å. Therefore R_k should be, at least, about 170 Å. These two calculations are not inconsistent, and we choose R_k to be about 200 Å as an approximate value.

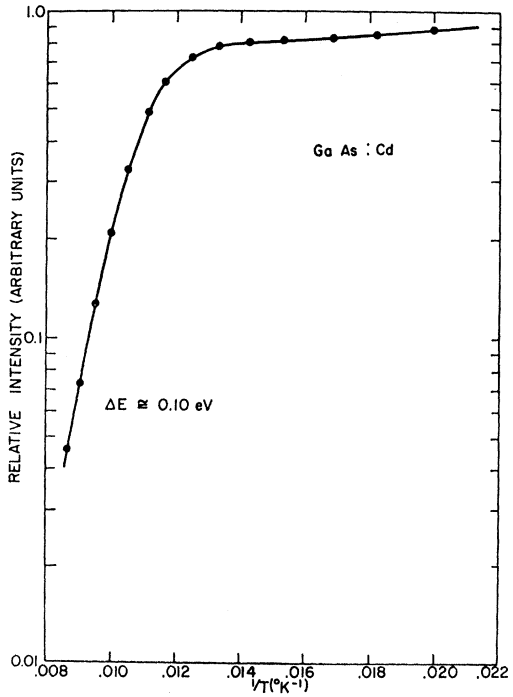

FIG. 8. Relative emission intensity versus reciprocal temperature ($°K^{-1}$) for the Cd 0 line of annealed irradiated GaAs:Cd.

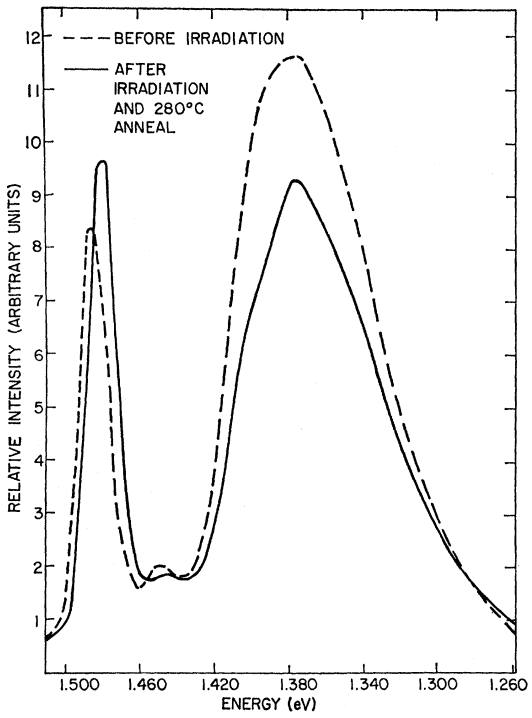

FIG. 9. Relative intensity of the near-band-edge and broad-band luminescence peaks versus photon energy in GaAs:Cd both before irradiation and after irradiation (1.5 MeV, $\varphi=5\times10^{16}$ e/cm^2) followed by 15-min anneals between 50 and 280°C.

Radiation-Induced Energy Shifts of the Lasing Transition and the Broad-Band Emission Peak

Figures 4 and 5 show that both the broad-band emission and the B' transition shift in energy with electron fluence. The shift is to higher energies for the lasing transition and to lower energies for the broad-band emission. Specific models for the luminescing centers must give an explanation of these observed energy shifts. It is known[7] that electron irradiation produces changes in the band edge, presumbly by a tailing of the density-of-states distribution in a manner similar to that resulting from the introduction of impurities.[8] The relatively low electron fluence is not expected to produce large changes of this type. No energy shifts resulting from similar fluences in GaAs with other dopants and in relatively pure material have been noted. In any case, an energy shift of emission due to this factor would

[7] H. Reiss, C. S. Fuller, and F. J. Morin, Bell System Tech. J. 35, 535 (1956).

[8] L. W. Aukerman, P. W. Davis, R. D. Graft, and T. S. Shilliday, J. Appl. Phys. 34, 3590 (1963).

always be toward lower energies and would not explain the high-energy shift of the B' transition.

Of the various radiative recombination mechanisms only donor-acceptor pair transitions allow a reasonable interpretation of the observed energy shifts, assuming that the emission peaks are envelopes of unresolved pair transitions. For example, a uniform (with respect to pair separation) decrease in the concentration of donor-acceptor pairs should result in a shift of the emission envelope to lower energies because the average separation between donors and acceptors will increase.[9] On the other hand, if the concentration of distant pairs is decreased relative to the concentration of more closely spaced pairs, the emission envelope will shift to higher energies.

Let us examine the killer center volume concept for its applicability in explaining the energy shifts when doner-acceptor pairs are quenched. The photon emission energy for electron-hole annihilation for pairs separated by a distance r is given by $h\nu = E_g - (E_A + E_D) + e^2/\epsilon r$, where E_A and E_D are the ionization energies for the acceptor and the donor, respectively, and E_g is the band-gap energy. An estimate of $E_A + E_D$ can be obtained by noting the emission energies for very large pair spacing. An extrapolation of the low-energy tail for the B' lasing transition, for example, gives an energy of about 1.47 eV. Since the band-gap energy is about 1.52 eV, and $E_A = 0.021$ eV for Cd,[10] this implies that $E_D \cong 0.029$ eV.

Silicon is a common impurity in GaAs and is found in these samples to be in the same concentration as Cd. Below concentrations of about $10^{18}/\text{cm}^3$, silicon acts as a donor and is located on gallium sites.[11] Williams and Blacknall[12] have measured the binding energy for silicon in GaAs by means of optical emission and find $E_D \cong 0.028$ eV. [*Note added in proof.* Williams (private communication) believes this ionization energy corresponds to the Si acceptor level. If so, the donor in question may involve Si in a more complex center or it may be an intrinsic lattice defect.] Thus, Cd-Si pairs seem plausible for producing the B' emission envelope. A hydrogenic model for the donor and acceptor, using the above values of ionization energies, allows an effective mass to be estimated and a Bohr radius for the electron and hole orbits to be calculated. For the B' transition, this gives an orbit radius of roughly 25 Å for Cd and 20 Å for Si.

Donors or acceptors within the killer center volume will be rendered incapable of participating in donor-acceptor pair transitions. If the sum of the donor and acceptor electron and hole radii is very much less than R_k, then the "edge" effects, i.e., the quenched luminescence of centers one of whose components lie outside the killer center volume, will be small. If this criterion is not met, the edge effects will be increased and more of the distant pairs will be quenched by the killer center volume relative to closely spaced pairs. This would cause the emission peak to shift to higher energies with increasing electron fluence as is observed for transition B'.

Based on the criterion above, the argument for donor-acceptor transitions for the near-band-edge luminescence would be rather weak in view of the estimates of killer center radius and the radii of the presumed donors and acceptors. The observed shift to lower energies with decreased excitation intensity, however, supports this viewpoint. The initial decrease in intensity with electron fluence below $\varphi = 1 \times 10^{16}\ e/\text{cm}^2$ is mirrored by the initial shift to higher energy shown in Fig. 5, and reflects the fact that the number of distant pairs affected is larger in the early stages of irradiation than is the case when the killer center volumes begin to overlap.

The deeper broad-band emission center can be treated in the same way. A measurement of the low-energy intercept of the Cd 0 line gives a value of about 1.35 eV. If we assume the same donor center as for the 1.48-eV transition then the value of E_A should be about 0.14 eV. The results of Fig. 8 are in fair agreement with this value. For such a deep acceptor a hydrogenic model does not apply, but it is apparent that the acceptor orbit will be small compared to the donor orbit. In this case, the value of R_k is large compared to the sum of the donor and acceptor radii and the killer center volume will quench luminescing centers uniformly with respect to separation of the individual pairs. We expect that, for this case, the peak of the distribution will move to lower energies as is observed in Fig. 4. Since the position of the broad-band emission is unique to the presence of Cd, we assume that Cd in a different charge stage is the acceptor involved. Any energy shift of the broad-band envelope on the basis of weakened lattice coupling brought about by irradiation would be negligibly small and would be toward higher energies.

Emission Changes due to Isochronal Annealing

Following irradiation at 80°K, no changes in luminescence were noted for anneals in the range 80°K–50°C. Vook[13] has studied the changes in thermal conductivity of high purity n-type GaAs brought about by low-temperature electron irradiation and has shown that the damage anneals out as point defects below 50°C while above 50°C the point defects form clusters. Potts and Pearson[14] have performed experiments on quenched-in defects in n-type GaAs and have shown by annealing studies of changes in lattice parameter

[9] J. Lefevre, D. Bois, P. Pinard, F. Davoine, and P. Leclerc, J. Opt. Soc. Am. **58**, 1230 (1968).

[10] D. Meyerhofer, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Academic Press Inc., New York, 1961).

[11] O. G. Lorimor and W. G. Spitzer, J. Appl. Phys. **37**, 3687 (1966).

[12] E. W. Williams and D. M. Blacknall, Trans. AIME **239**, 387 (1967).

[13] F. L. Vook, Phys. Rev. **135**, A1742 (1964).

[14] H. R. Potts and G. L. Pearson, J. Appl. Phys. **37**, 2098 (1966).

that there is a rapid annealing at room temperature and a slower anneal near 200°C with an activation energy of about 1.0 eV. Their experiments on samples grown with increasing As overpressure clearly indicate that the 200°C annealing stage corresponds to the movement of As vacancies. The rapid room-temperature annealing is in agreement with the results of Vook,[13] who found that 70% of the induced changes in thermal conductivity annealed out below 50°C and presumbly represent interstitial annealing by close-pair recombination and by trapping at structural defects or impurities. This low-temperature annealing begins as low as 55°K.

The existence of an annealing stage near 200°C in electron-irradiated GaAs has also been shown by Aukerman and Graaft[15] for recovery of electrical conductivity and by Vook[16] for recovery of length change. Aukerman and Graaft find, for p-type GaAs, that the damage anneals out in three stages centered about 155, 240, and 350°C. The 240°C stage is characterized by an activation energy of about 1.0 eV and presumably is the migration energy for vacancies, in agreement with the results of Potts and Pearson. Aukerman and Graaft had originally believed this stage represented close-pair recombination, but the results of Vook and of Potts and Pearson make this interpretation questionable. Aukerman and Graaft find that 90% of the damage annealed out in the 155 and 240°C stages.

In the present experiment, Fig. 7 shows the buildup of emission of the Cd 0 line and its replicas between 50 and 190°C after which the intensity diminishes. The B' transition is not changed in this temperature range. This corresponds roughly to the stage centered about 155°C noted by Aukerman and Graaft. In this annealing temperature range, Vook[13] noted the formation of minima in GaAs thermal conductivity curves which indicated the presence of resonant scattering from localized modes. Such interactions serve to decrease the coupling of other centers to lattice vibrations and account for the increased resolution of the Cd 0 line and its phonon replicas in this temperature range.

The diminution of emission intensity of the Cd 0 complex above 190°C corresponds to a similar reduction of centers giving rise to localized modes in the thermal conductivity data.[13] Thus as the lattice coupling again increases the emission intensity diminishes. The sharp increase in the intensity of the Cd 0 complex at 240°C is accompanied by a loss of structure and a sudden increase in the B' transition. This stage presumably represents the annealing of the defect responsible for the degradation of luminescence.

[15] L. W. Aukerman and R. D. Graft, Phys. Rev. **127**, 1576 (1962).

[16] F. L. Vook, J. Phys. Soc. Japan **18**, Suppl. II, 190 (1963).

It was shown in earlier work[2,5] that the displacement of the group-V element in III-V compounds was more effective in quenching luminescence than was the displacement of the group-III component. Goldstein[17] has shown that the energy of self-diffusion of the group-V element is always greater than that of the group-III element in the III-V compounds and that the diffusion takes place via the respective sublattice. We can thus tentatively identify the 155°C stage with the migration of Ga vacancies which cluster and form localized modes, and the 240°C stage with the annealing of As vacancies which have acted as killer centers.

CONCLUSIONS

The near-band-edge lasing emission of boat-grown GaAs:Cd has three transitions (A', B', C') at 1.507, 1.486, and 1.484 eV. The temperature dependence of the intensity of these transitions is very similar to that of the three near-band-edge transitions observed in GaAs:Zn and show that these lines are due to transitions from three excited states to a ground state. The upper levels (B' and A') are thermally depopulated at low temperatures. Fast-electron irradiation of GaAs:Cd results in degradation of luminescence and energy shifts of the B' lasing transition (dominant at 25°K) and a broad-band emission peak near 1.37 eV. The high-energy shift of the former, the low-energy shift of the latter, and the exponential decrease in intensity with electron fluence can be explained on the basis that both bands represent donor-acceptor pair emission envelopes and that emission is quenched by a displacement event which kills all luminescing centers within a finite volume. Neutral cadmium and an unknown donor, possibly silicon, is believed to be the center responsible for the near-band-edge luminescence while the same donor with Cd in a different charge state gives rise to the broad-band emission. On the basis of isochronal annealing results, the broad-band emission is interpreted to be due to the phonon replication of a donor-acceptor pair envelope (Cd 0 line) peaking at 1.369 eV. The resolution of the structure is due to weakened lattice coupling brought about by the formation of localized modes. These localized modes could be due to the clustering of Ga vacancies which form precipitates as the temperature is increased. The killer centers anneal out at 240°C and are presumed to be As vacancies.

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[17] B. Goldstein, Phys. Rev. **121**, 1305 (1961).