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Radiative Recombination in Annealed Electron-Irradiated GaAs*

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Broad-band emission peaking near 1.39 eV appears in Zn-doped GaAs in addition to the narrow bound-exciton emission at 1.49 eV. Electron irradiations at energies between 0.6 and 2.0 MeV for time-integrated fluxes of 1.3×10^{18} e/cm^2 quench all luminescence. For bombardment energies below a critical value, which lies between 1.0 and 1.5 MeV, isochronal annealing near 190°C causes the reappearance of the broad-band emission, which now is found to possess structure. The structure consists of three no-phonon lines at 1.4433, 1.4415, and 1.4402 eV which are repeated at intervals of the transverse acoustic phonon energy. The emission intensity is greatest for temperatures near 220°C. Further annealing at higher temperatures diminishes the intensity of the fine structure and the associated broad-band emission; complete disappearance occurs above 260°C. The emission is not regained upon annealing when the bombardment energy exceeds the critical value. It is suggested that direct lattice displacement occurs at the critical bombarding energy. This would correspond to a threshold displacement energy of 50–60 eV. It is also suggested that previous measurements of threshold energy (10–20 eV) in GaAs and other experimental observations may be due to known large concentrations ($\approx10^{19}$ cm^3) of defects in as-grown GaAs, in the form of Ga-As interstitial pairs.

THIS article describes the appearance of sharp-line emission spectra in GaAs resulting from electron irradiation followed by annealing. The development of the spectra is particularly remarkable because of its sensitivity to the irradiation-electron energy. Previous work[1] on the degradation of luminescence by electron irradiation (340 keV–2 MeV) showed that the emission intensity decreases exponentially with time-integrated flux ($\lesssim10^{17}$ e/cm^2) and that the decrease is greatest when the electrons are incident on $(\bar{1}\bar{1}\bar{1})$ faces. These data were interpreted to suggest that As defects produced by electron irradiation migrate to the luminescent centers and quench the luminescence. In the present study, the effects of displacement per se were investigated by using much larger time-integrated fluxes (1.3×10^{18} e/cm^2) in all irradiations in order that the generated defects would be in excess of the dopant concentration. Fluxes of this magnitude were found to eliminate completely all luminescence in GaAs for the investigated electron energies between 0.6 and 2.0 MeV. The effects noted here were found to be the same for bombardment of either $(\bar{1}\bar{1}\bar{1})$ or (111) faces, although most of the irradiations were made with $(\bar{1}\bar{1}\bar{1})$ faces exposed to the electron beam. The effect was not investigated with the electron beam incident on other crystal planes.

The data reported here were obtained from Zn-doped GaAs having hole concentrations of $\sim10^{17}$/cm^3. Typical emission at 4.2°K from as-grown material is shown by the dashed line in Fig. 1. The peak at 1.49 eV is that responsible for laser action in GaAs diodes. The broad emission centered about 1.39 eV has been previously observed by Nathan and Burns[2] and Turner *et al.*,[3] but its origin was not determined. Similar broad-band emission is seen in n- and p-type GaAs but not in high-purity (n-type) material. The peak position varies for n- and p-type GaAs but does not seem to depend on the specific dopant.

Isochronal annealing in the temperature range 190–220°C of a sample irradiated at 0.6-MeV electron energy, brings about the reappearance of the broad-band emission together with new sharp-line structure as shown in Fig. 1. Details of the structure are shown in the inset. The three sharp ($\approx5\times10^{-4}$ eV) no-phonon lines (A,B,C) at 1.4433, 1.4415, and 1.4402 eV are repeated at spacings of 0.011 eV, which is equal to the transverse acoustic (TA) phonon energy. Emission of up to 8 phonons has been resolved. The intensity of the sharp-line spectrum becomes a maximum after anneal-

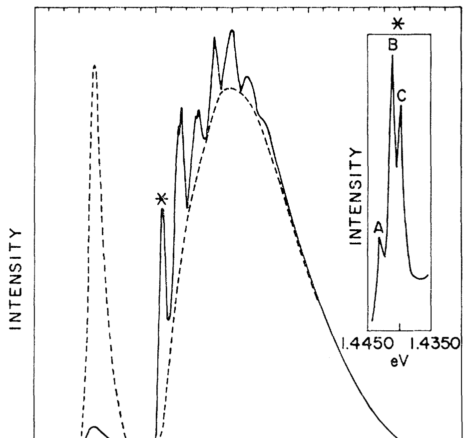

FIG. 1. Emission intensity at 4.2°K for Zn-doped GaAs (3.8×10^{17} holes/cm^3) versus photon energy. Dashed line represents intensity before irradiation; solid line represents intensity after 0.6-MeV electron irradiation followed by 15-min anneals at 190, 200, and 210°C. Details of the fine-line structure near 1.44 eV are shown in the inset.

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[1] G. W. Gobeli and G. W. Arnold, Bull. Am. Phys. Soc. **10**, 321 (1965).

[2] M. I. Nathan and G. Burns, Phys. Rev. **129**, 125 (1963).

[3] W. J. Turner, G. D. Pettit, and N. G. Ainslie, J. Appl. Phys. 34, 3274 (1963).

ing to about 220°C. Annealing at higher temperatures decreases the intensity, and the emission disappears above 260°C. For the same temperature range (200–250°C), Aukerman and Graft[4] found that electrical conductivity changes in GaAs brought about by 1.0-MeV irradiations annealed out, and Vook[5] found a lattice contraction in studies of length changes brought about by irradiation at 1.6 and 2.0 MeV.

Irradiations at several electron energies show that this sharp line spectra cannot be formed on annealing (for temperatures up to 350°C) when the incident electron energy is above a critical value which falls between 1.0 and 1.5 MeV. Annealing of unirradiated material also does not result in the fine-line spectra. It was found that the temperature of the sample during irradiation was not of importance in the subsequent development of the spectra. Irradiations were performed at 45 and 296°K with no apparent differences in results.

A precise investigation of the intensities of the fine lines as a function of measuring temperature has not been carried out, but the spectra are unobservable at measuring temperatures not greatly in excess of 40°K. Measurements made on a sample while cooling to 4.2°K indicate that line A decreases in intensity with decreasing temperature while lines B and C increase. This variation in relative intensities with temperature suggests that the three lines of the sharp-line spectrum arise from the same defect[6] and are probably not due to donor-acceptor pair emission. Such emission furthermore, seems to be unlikely since only three lines can be resolved. The spectra have distinct similarities to the bound exciton emission observed in ZnTe.[7] In that case, state splitting by electron-hole jj coupling was invoked to give an allowed transition to the $J=1$ state and a forbidden transition to a $J=2$ state with a third broader peak representing transition from $J=2$ to $J=1$ with virtual-phonon emission. In the present case, however, all three peaks have the same width, and all peaks remain distinct from 4.2 to 40°K, in contrast to ZnTe where the allowed transition alone is present at higher temperatures.

GaAs is known to have many defects ($\approx 10^{19}/\text{cm}^3$) in the as-grown state[8–10] which can be detected after high-temperature annealing (>700°C). These defects have not been positively identified, although there is considerable evidence that they are intrinsic defects. Such large numbers of defects in GaAs could well explain the low displacement-threshold values reported by Bauerlein[11] of 9–10 eV. Grimshaw and Banbury[12] found values of about 17 eV by different techniques and were not able to confirm Bauerlein's measurements. Measurements by Vook[5] have indicated that for large time-integrated fluxes, the effective threshold displacement value may be near 45 eV. Growth variations in synthetic quartz[13] are known to result in similar changes (15–50 eV) in threshold energy values, and the disorder in CdS is also believed[14] to cause changes in threshold values. These considerations lead to the suggestion that the critical electron bombardment energy found in the present investigation is that energy at which intrinsic lattice displacement occurs, and that effects at lower energies involve interaction with built-in defects. The critical energy for this presumed intrinsic displacement is not precisely known, but the measurements reported here would indicate a value of 50–60 eV.

Interstitial Ga-As electrically neutral pairs are an attractive possibility as models for the defects in as-grown material. Many observations could be explained since the separation of these pairs could be accomplished by single bond breaking at relatively low electron energies and at temperatures of the order of 700°C.[8,10] Separated interstitials would produce changes in electrical conductivity and could bring about the luminescence degradation. In addition, the orientation of the pairs would predict As atoms to be preferentially displaced by irradiations on $(\bar{1}\bar{1}\bar{1})$ faces. The nonappearance of the fine-line spectra at higher electron energies could result from the formation of nonradiative aggregates which involve displaced lattice constituents. This view is supported by the observation that a sample irradiated at 0.6 MeV followed by an irradiation at 2.0 MeV did not yield the fine-line spectra when annealed.

The specific nature of the defect giving rise to the emission has not been determined. The position of the lines indicate an ionization energy for the defect of about 0.08 eV, which does not correspond to any of the known defect levels in GaAs. Further experiments with stressed samples and magnetic fields are necessary to identify the defect responsible for the emission.

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

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

[6] D. G. Thomas, M. Gershenzon, and J. J. Hopfield, Phys. Rev. **131**, 2397 (1963).

[7] R. E. Dietz, D. G. Thomas, and J. J. Hopfield, Phys. Rev. Letters **8**, 391 (1962).

[8] J. Blanc, R. H. Bube, and L. R. Weisberg, Phys. Rev. Letters **9**, 252 (1962).

[9] B. Goldstein and N. Almeleh, Appl. Phys. Letters **2**, 130 (1963).

[10] J. Blanc, R. H. Bube, and L. R. Weisberg, J. Phys. Chem. Solids **25**, 225 (1964).

[11] R. Bauerlein, in *Proceedings of the International School of Physics, Radiation Damage in Solids* (Academic Press Inc., New York, 1962), p. 358.

[12] J. A. Grimshaw and P. C. Banbury, Proc. Phys. Soc. (London) **84**, 151 (1964).

[13] G. W. Arnold, Phys. Rev. **140**, A176 (1965).

[14] G. F. J. Garlick, F. J. Bryant, and A. F. J. Cox, Proc. Phys. Soc. (London) **83**, 967 (1964).