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Luminescence in Zn-Doped GaAs†

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Broad-band emission in Zn-doped GaAs centered near 1.38 eV shows sharp-line structure when the material is electron-irradiated near room temperature and annealed near 200°C. The broad band occurs because of phonon replication of three sharp lines (A,B,C) of about 5×10^{-4} eV width which are centered about 1.44 eV. Measurements of the broad- and sharp-line intensity as a function of temperature, excitation intensity, and uniaxial stress have shown that the sharp-line spectrum is due to the annihilation of a bound exciton. It is suggested that the exciton is bound at a complex involving Zn^- and a lattice defect (i.e., vacancy or interstitial).

INTRODUCTION

RADIATIVE recombination in GaAs may occur, and has been observed, through free-exciton recombination, free-to-bound transitions, and bound-exciton annihilation. In addition to spectra of this type, where the line width is at most of the order of kT, broad-band luminescence is found in most materials. This type of luminescence has a half-width of the order of 0.2 eV, and the peak position may lie between 0.65 and 1.39 eV. Some of these broad-band luminescence peaks have been studied in sufficient detail to identify the defect giving rise to the radiative transition. Two peaks centered near 1.35 and 0.95 eV have been rather firmly established[1,2] as being due to Cu impurity. In n-type GaAs (Te, C, Si, Ge, Sn, S, Se), broad-band emission near 1.2 eV has been associated[3] with a lattice vacancy and a nearby donor. A broad band near 0.65 eV increases in intensity when crystals are grown under increased oxygen pressure.[4]

Zn-doped GaAs has a broad-band emission peak centered near 1.38 eV. Experiments in which such samples have been irradiated with electrons in the energy range of 0.5 to 1.5 MeV followed by annealing near 200°C have shown[5] that the broad-band emission is due to three sharp-line transitions near 1.44 eV accompanied by multiple phonon emission. The present paper utilizes the temperature- and excitation-intensity dependence of the emission and uniaxial stress measurements to further identify this defect.

EXPERIMENTAL

Zn-doped GaAs with carrier concentrations of the order of $10^{17}/\text{cm}^3$ grown by Bell & Howell Research Center and Monsanto Corporation were investigated. Sample surfaces were treated with a bromine-alcohol etch. Emission was optically excited by chopped light from an HB-200 mercury arc. Initial filtration was with a $CuSO_4$ solution. The emission was observed from the surface exposed to the exciting light. After further appropriate filtration, the emission was scanned by a Perkin-Elmer 210 grating spectrometer and detected by a cooled RCA 7102 photomultiplier, amplified, and recorded on an X-Y recorder.

Two Dewars were used in obtaining the data. For some of the temperature-dependence studies a stainless-steel Dewar with the sample mounted on a cold finger was employed. Controlled temperatures from 30°K to above room temperature could be obtained with the use of a sample block heater and a set-point temperature controller. For the stress measurements and some of the temperature-dependence measurements, a Martin glass Dewar was used, and the sample was cooled either by direct immersion in liquid He or by the boil-off He gas from a large helium storage container. The sample temperature was sensed and controlled by a thermocouple and heater circuitry.

Stress was applied by gas pressure from a standard delivery tank applied through a regulator valve to a driving piston and then to the sample. The apparatus is shown schematically in Fig. 1. With a ratio of 10^3 between piston area and sample area, sample stresses of 10^5 lb/in.^{2} or about 7×10^3 kg/cm^2 could be applied with a standard 0 to 100 lb/in.^{2} regulator valve. Pistons of other sizes could be employed to extend or decrease this range. This type of apparatus is particularly advantageous for optical measurements since the sample position need not be accidentally changed as is often the case in devices employing incremental loading or when stress is applied by a screw-threaded shaft.

RESULTS AND DISCUSSION

The photoluminescence spectrum of Zn-doped GaAs before and after room-temperature electron irradiation and annealing near 200°C is shown in Fig. 2. The details of the process required to generate the sharp-line structure have been given in earlier work.[5] The broad band is always centered near 1.39 eV in Zn-doped samples. Other dopants result in broad bands at other energies, e.g., in Cd-doped material the peak is at 1.37 eV and in S-doped samples it is at 1.22 eV. Similar

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[1] H. J. Queisser and C. S. Fuller, J. Appl. Phys. **37**, 4895 (1966).

[2] T. J. Larsen, Appl. Phys. Letters **3**, 113 (1963).

[3] E. W. Williams, Phys. Rev. **168**, 922 (1968).

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

[5] G. W. Arnold, Phys. Rev. **149**, 679 (1966).

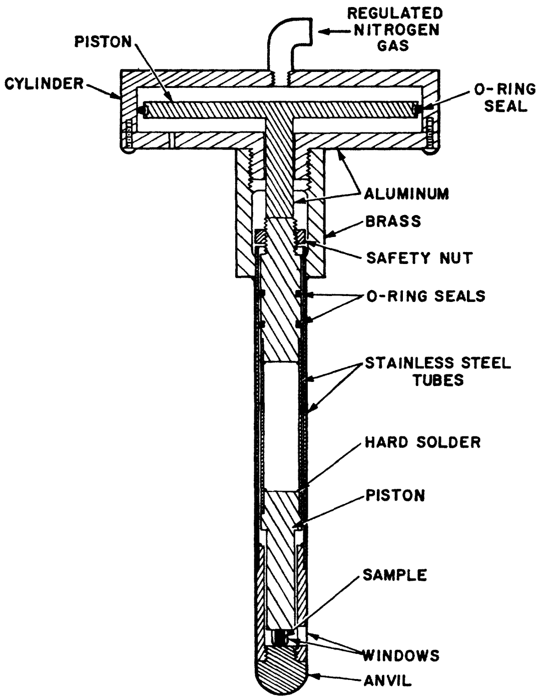

FIG. 1. Cross-section schematic of uniaxial stress apparatus.

shifts are noted for other *n*- and *p*-type dopants. Broad-band emission is usually not found in relatively high purity Czochralski or in Zn-doped epitaxially grown GaAs. The lasing transition near 1.49 eV shown in Fig. 2 has been studied extensively, and there is general agreement that the transition is due to electron capture by a neutral acceptor. The substitutional Zn dopant would provide a suitable terminal point for this transition.

The temperature dependence of the integrated broad-band intensity was measured to determine whether or not the superposition of the structure on this spectrum was coincidental. From the plot of intensity versus $1/T$ shown in Fig. 3, a single activation energy of 0.082 eV can be computed. This "activation" energy compares favorably with the energy difference of 0.08 eV between the first (highest energy) line 1.44 eV in the developed structure and the band-gap energy of 1.52 eV. This strongly suggests that the broad-band luminescence is due to transitions at an energy of 1.44 eV with a broadening and a shift of the intensity peak to 1.39 eV due to strong coupling to the lattice. This is further confirmation that the structure on the broad band is associated with phonon-assisted transitions at the same type of center which gives rise to the broad-band emission.

The broad-band emission intensity has also been measured as a function of the excitation intensity. These results are shown in Fig. 4 for temperatures of 48 and 81°K. These temperatures were chosen to be representative of the two distinctly different temperature regions of Fig. 3. For the lower temperature, the emission intensity varies linearly with excitation intensity at low intensities, the dependence becoming sublinear at higher-excitation intensities. At 81°K, where thermal quenching of the luminescence is taking place, the variations in emission intensity are quadratic and linear for the low- and high-excitation intensities, respectively. Maeda[6] has obtained similar results for emission in GaP which

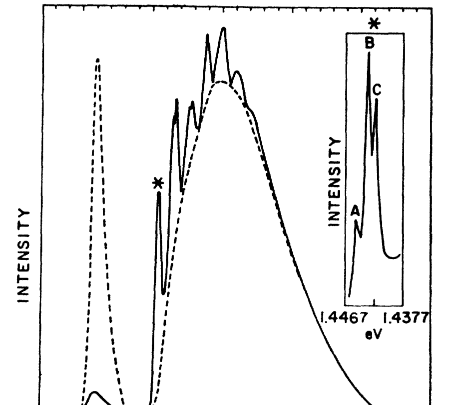

FIG. 2. Emission intensity at 25°K for Zn-doped GaAs (3.8×10^{17} holes/cm^3) versus photon energy. Dashed line represents intensity before irradiations; solid line represents intensity after 0.6-MeV electron irradiation followed by 15-min anneals at 190, 200, and 210°C. Details of the fine-line structure near 1.44 eV are shown in the inset.

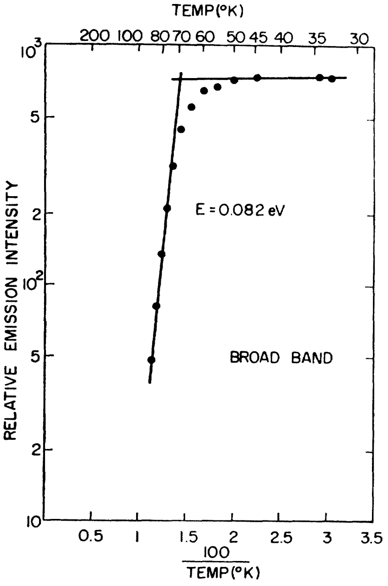

FIG. 3. Logarithm of the broad-band emission intensity for Zn-doped GaAs versus reciprocal temperature.

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[6] K. Maeda, J. Phys. Chem. Solids **26**, 595 (1965).

is known to arise from donor-acceptor pair transitions. The results in Fig. 4 do not, however, uniquely determine a model for the recombination.

At the measurement temperatures the carrier concentrations should depend, for the most part, on the creation and recombination rates rather than on the thermal equilibrium concentrations. Under these conditions, for low-carrier concentrations, recombination should be dominated by killer centers in the material, and the electron and hole concentrations would be linear in the excitation intensity. At higher-carrier concentrations, direct recombination could be expected to dominate, and the carrier concentrations would then each vary as the square root of the excitation intensity. At still higher concentrations impact (or Auger) recombination might dominate, and the carrier concentrations would vary as the cube root of the excitation intensity. If the observed luminescence is due to bound-exciton annihilation, then we might expect the emission intensity to vary as the product of the electron and hole concentrations. In this case, for the three intensity ranges this would give quadratic, linear, and $\frac{2}{3}$ power dependences, respectively, for the luminescence intensity as a function of excitation intensity. The exact locations of these three intensity ranges would depend on the various capture and thermal release cross sections involved in the process and would be expected to be different for different temperatures.

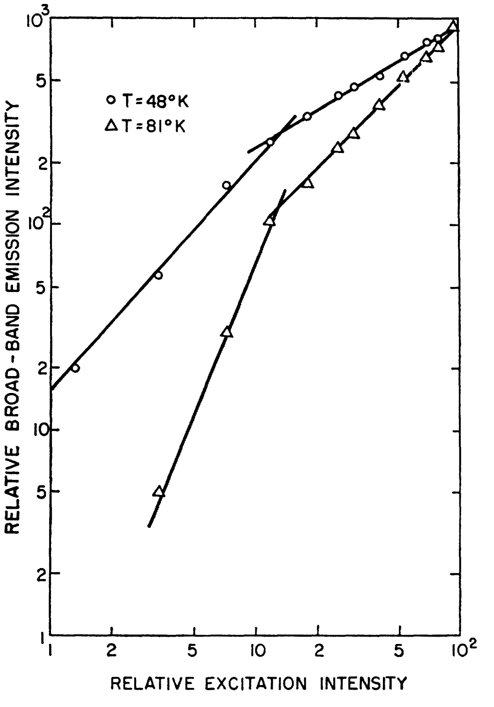

FIG. 4. Logarithm of relative broad-band emission intensity for Zn-doped GaAs versus logarithm of relative excitation intensity at $T=48$°K and $T=81$°K.

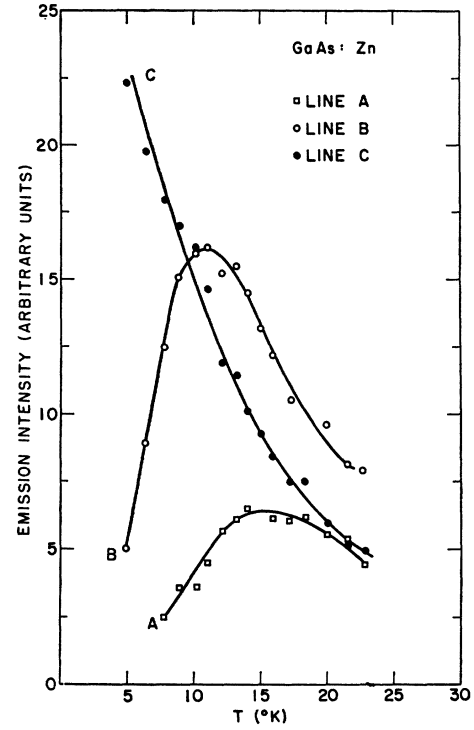

FIG. 5. Relative emission intensity versus temperature for lines A, B, and C in Zn-doped GaAs after electron irradiation and annealing to 200°C.

The sharp three-line spectrum which appears after electron irradiation and annealing is replicated at energy increments of 0.036 and 0.011 eV. The former energy is the LO lattice phonon energy, and the latter corresponds to the TA phonon energy. In order that this structure appear, the effective coupling of the center to the lattice must be decreased by the irradiation and annealing treatments. While it is not clear exactly how this happens, it seems likely that these treatments create localized lattice modes at damage sites away from the luminescent centers thereby reducing the effective phonon density of states at these centers. The sharpness of the three lines resolved in these spectra identifies the luminescence as resulting from bound-to-bound transitions in the solid, because free-to-bound or free-to-free transitions would show an energy spread of $\sim kT$.

The temperature dependence of the sharp-line spectra is shown in Fig. 5. Lines A and B (Fig. 2) are seen to grow with increasing temperature, line B reaching a peak value near 11°K and then decreasing while line A peaks near 15°K. Line C decreases in intensity over the range 5 to 110°K. This variation in intensity with temperature indicates that transitions at a single defect center involving recombination between three excited states and a ground state are responsible for the observed luminescence. The upper two excited states are depopulated at the lowest temperatures. It has recently[7] been shown that the three-component Zn

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[7] G. W. Arnold and D. K. Brice, Appl. Phys. Letters **13**, 51 (1968).

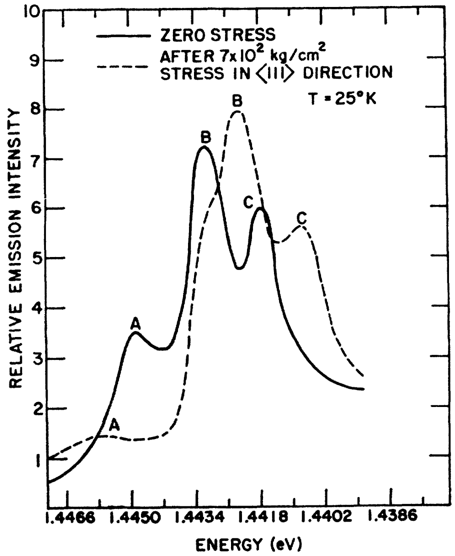

FIG. 6. Relative emission intensity of sharp-line spectra versus photon energy before and after application of uniaxial stress in ⟨111⟩ direction. $T=25$°K.

lasing transition near 1.49 eV behaves in a similar fashion with temperature. This lasing luminescence involves transitions from three excited states to a single ground state, the upper state being an electron in or near the conduction band (similar to the F' center) or in a shallow donor state. The splitting of the upper levels then results from the j-j coupling of the $s_{1/2}$ electron with the $p_{3/2}$ hole on the neutral acceptor and crystal-field interaction with the lattice.

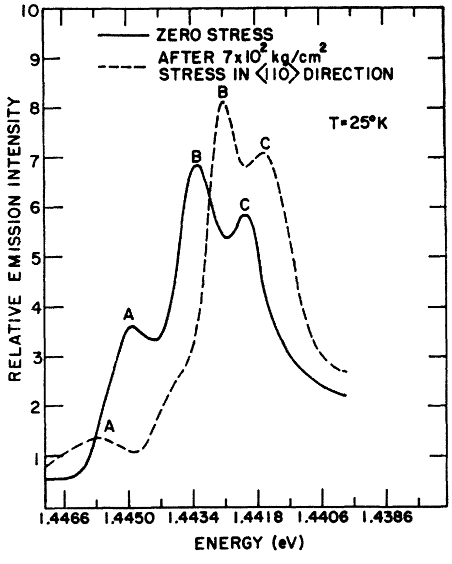

FIG. 7. Relative emission intensity of sharp-line spectra versus photon energy before and after application of uniaxial stress in ⟨110⟩ direction. $T=25$°K.

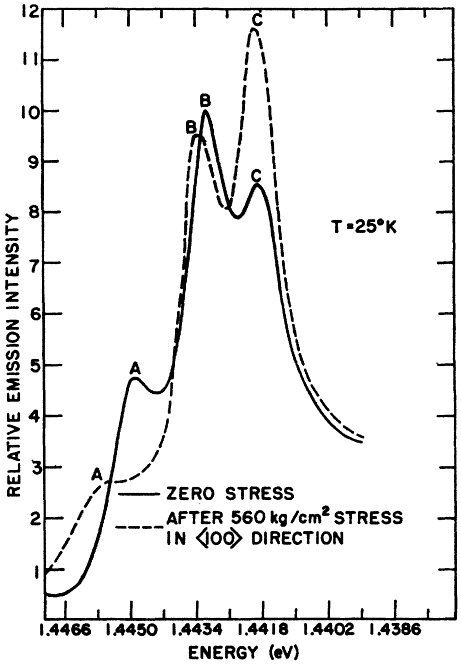

FIG. 8. Relative emission intensity of sharp-line spectra versus photon energy before and after application of uniaxial stress in ⟨100⟩ direction. $T=25$°K.

Uniaxial stress measurements were made on samples (0.125×0.125×0.250 in.) which had been irradiated on all major surfaces at the same energy and fluence (1.5 MeV; 2×10^{17} e/cm^2) and annealed to bring out the sharp-line spectra. Measurements were made of the emission spectra for stress applied along the ⟨111⟩, ⟨110⟩, and ⟨100⟩ directions at $T=25$°K. The results are shown in Figs. 6, 7, and 8 for the spectra obtained for the unstressed and the maximum stress conditions. A few general observations can be made for these spectra. One of these is that there is a large decrease in intensity and a shift to higher energy of line A in all three cases. The pressure coefficient of the band gap energy is about 10^{-5} eV/kg/cm^2 so that for the maximum stress applied here, the shift in E_g should be of the order of 10^{-2} eV. The shift in energy of line A is in the same direction, but an order of magnitude smaller than the band gap energy shift. Secondly, lines B and C show little or no energy shift under uniaxial stress in a ⟨100⟩ direction, but shift to lower energies under uniaxial stress in the ⟨111⟩ and ⟨110⟩ directions. The shifts are larger for ⟨111⟩ stress, but in both cases are of the same order of magnitude as the energy shifts for line A. Finally, there is little or no broadening of the lines of the spectrum except for the appearance of a shoulder on line B for ⟨111⟩ and ⟨110⟩ stress.

The generally small stress-induced energy shifts indicate that the stress potentials for this center are an order of magnitude smaller than the corresponding potentials for the valence band. This is not surprising in view of the tight binding (0.08 eV) of the center. The shoulder on line *B* at the highest stress values represents the onset of stress-induced splitting of the lines of the spectrum, in analogy with the stress-induced splitting of the valence band states. However, the small stress potentials indicated above preclude resolution of the splitting over the stress range of our experiments. The detailed analysis of the energy and intensity shifts will be dealt with elsewhere.[8]

CONCLUSIONS

The evidence thus far presented permits us to associate the luminescence with bound-to-bound transitions involving a Zn substitutional impurity. Furthermore, the similarity between the 1.49-eV lasing luminescence and the sharp-line spectra at 1.44 eV suggests that the three excited states of the latter transition are due to the *j-j* coupling of an $s_{1/2}$ electron and a $p_{3/2}$ hole. The two simplest centers for the sharp-line spectra which satisfy these conditions are donor-acceptor pair recombination and bound-exciton recombination.

A number of points argue against the donor-acceptor pair model. While any one of these points by itself would not be sufficient to rule out the pair model, together they form a strong argument against its acceptance. First, there are only three lines in the spectrum. Normally, there are a large number of lines in the pair spectrum reflecting the multiplicity of donor-acceptor separations in the lattice. Second, the temperature dependence of the intensities suggests that the three excited states are located at a single center. Third, considering the electrostatic energy contribution to donor-acceptor luminescence both the energy positions of lines *A*, *B*, and *C* and the generally small amount of stress-induced broadening mean that the pairs must be separated by a distance greater than 8 Å. In addition, the stress-induced energy shifts mean that pairs corresponding to lines *B* and *C* must be separated along a ⟨111⟩ direction. It is difficult to imagine *only* three stable donor-acceptor pair separations of greater than 8 Å, two of which must lie along a ⟨111⟩ axis. This model is thus unable to account for the observed properties of the luminescence.

Group-theoretical analysis of the exciton bound at a Zn-impurity site shows that for T_d symmetry or lower, and for all plausible charge states of the Zn impurity, only the exciton trapped at a Zn^- site can give the three excited states and single ground state required by the data. For T_d symmetry, two of the transitions are forbidden. The forbidden transitions may be observed, however, because they lie at lower energies, thereby allowing the relevant levels to become heavily populated. On the other hand, the local symmetry of the center may be reduced from T_d. There are three allowed transitions for the D_{2d} reduction in this symmetry. [*Note added in proof.* Dingle of Bell Telephone Laboratories has recently examined one of our samples using higher resolution than that of our equipment. He finds that line *C* consists of two closely spaced lines of approximately equal intensity, and he observes a very weak line just to the high-energy side of line *B*. An exciton trapped at a center having C_{3v} symmetry (for which there would be four allowed transitions and one forbidden transition) would be consistent with these data.] Lower symmetry could be brought about by a number of mechanisms, including Jahn-Teller distortions, nearest-neighbor impurity atoms, etc. Because the broad-band emission is not seen in epitaxially grown GaAs, where the stoichiometry is expected to be better than in melt-grown material, it is probable that a lattice defect, most likely a vacancy, is a component of the center.

We conclude, therefore, that the luminescence results from bound exciton annihilation at a Zn^- impurity site. The three excited states in this case arise from the *j-j* coupling and crystal field splitting of the exciton levels.

ACKNOWLEDGMENT

These experiments have been greatly facilitated by the skill of Floyd M. McIver in the design of much of the equipment.

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[8] D. K. Brice and G. W. Arnold (to be published).