Recombination Radiation in GaAs

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Sharp-line emission near the absorption edge due to recombination of electrons and holes in recently available high-purity GaAs has been observed. At 4.2°K exciton emission is observed at 1.5143±0.0005 eV. The temperature dependence of this line is followed to 200°K and discussed. Below the energy gap a set of three lines is observed separated from each other by a longitudinal optical mode phonon energy (0.0364±0.0005 eV). In crystals grown in an O_2 atmosphere an emission is observed apparently due to recombination of a bound exciton. The intensity of this line relative to the exciton line increases with O_2 pressure and occurs 0.0015 eV below the exciton line.

INTRODUCTION

RADIATIVE emission due to the recombination of electrons and holes has been observed from many semiconductors. In silicon,[1] germanium,[1,2] silicon carbide,[3] and several 2–6 compounds[4] sharp line spectra near the energy gap have been seen. These spectra have been interpreted to give information concerning the band structure, the exciton structure, the phonon spectra, and the nature of the impurities in the material.

Much less detailed work has been carried out on the 3–5 compounds. Most of the work has been done using electrical injection at p–n junctions.[5–9] This typically results in a broad emission band (>0.1 eV) extending below the energy gap or sometimes in several broad bands. Recently, Pankove and Massoulie[9] have observed narrower emission lines (≈0.02 eV) from a GaAs junction. Also, sharp but complex spectra have been observed in GaSb by optical injection of carriers.[10]

Here, the measurement of recombination radiation in high-purity and doped GaAs is reported. Optical injection of carriers is used, and in the pure GaAs sharp lines are observed (as narrow as 0.0005 eV). One line is observed at the energy corresponding to the exciton absorption line[11] and is presumably due to the recombination of a free exciton. A second line is observed which is probably due to the recombination of an exciton bound to an impurity center. Also, several other lines are observed separated from each other by the longitudinal optical (LO) phonon energy. This behavior, which is seen in several 2–6 compounds,[4] has not been previously reported in 3–5 compounds. In doped crystals broad emission lines, characteristic of the previous junction GaAs measurements, have been observed by the optical injection method used here.

EXPERIMENTAL

High-purity GaAs was used, grown by Ainslie and Blum of this laboratory. These crystals have room- and liquid-nitrogen temperature mobilities higher than normally observed. The GaAs crystals were grown in two ways: (1) the Czochralski technique using a sealed puller with a magnetic chuck and an AlN crucible, (2) by the horizontal Bridgman technique under oxygen pressure. The undoped pulled crystals were n type and exhibited Hall mobilities between 17 000 and 23 000 $cm^2 V^{-1} sec^{-1}$ at 77°K (and up to 7800 $cm^2 V^{-1} sec^{-1}$ at room temperature) and electron concentrations between 10^{15}–10^{16} cm^{-3}. The crystals grown in an oxygen atmosphere had room-temperature electron concentrations which varied from 10^{16} to 10^8 cm^{-3} with increasing oxygen pressure. The Hall mobility of the crystals was as high as 30 000 $cm^2 V^{-1} sec^{-1}$ at 77°K (and up to 8500 $cm^2 V^{-1} sec^{-1}$ at room temperature). A description of the growth and electrical properties of these high-purity crystals has been published by Ainslie, Blum, and Woods.[12]

The emission measurements were performed with a Perkin–Elmer 99G grating monochromator having a dispersion of 27 Å/mm. at the energy gap of GaAs (~1.5 eV). A cooled Dumont 6911 photomultiplier and a PbS cell were used as detectors. A mercury arc filtered by a copper sulfate solution was used to excite the carriers.

The samples were lapped and then etched in dilute "white etch" so that the surface appeared shiny. The emitted radiation was observed from the same side of sample as the incident radiation. The latter was prevented from entering the spectrometer by baffling and filtering. The samples generally were immersed in the refrigerant (liquid He or liquid N_2). For measurements

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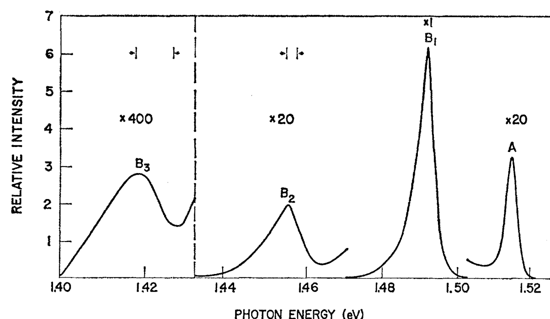

FIG. 1. Typical spectrum near the absorption edge of a GaAs crystal pulled from an AlN crucible, $T=4.2°K$. (The scale is linear in wavelength.)

between 4.2 and 65°K the samples were mounted on a copper block in an exchange gas and data were taken as the block warmed slowly. The sample temperature was measured by a carbon resistor mounted on the block.

RESULTS AND DISCUSSION

Figure 1 shows the emission spectrum of a typical pulled undoped (AlN grown) crystal at 4.2°K in the region of the absorption edge. Four lines are observed. The most intense line B_1 occurs at a photon energy of 1.4919 ± 0.0005 eV (0.0224 eV below line A).

Line B_2 is at a photon energy 0.0364 ± 0.0005 eV below line B_1. This energy separation is very close to the value of the longitudinal optical mode phonon energy obtained from measurements of optical absorption due to lattice vibrations[13] (0.0364 eV) and from tunnel diode measurements[14] (0.0349 eV). Line B_3 is approximately another optical mode energy below line B_1. The energy separation between B_2 and B_3 is 0.037 ± 0.002 eV.

The relative intensities indicated in Fig. 1 are typical of undoped grown AlN crystals. The relative intensities varied by about a factor of two among the undoped samples measured.

Figure 2 shows the edge emission spectrum of a sample of semi-insulating GaAs grown in an O_2 atmosphere. The gross similarity with Fig. 1 is evident: there are four lines at approximately the same photon energies. However, in Fig. 2 it is apparent that some of the lines have structure. The line B_1' has three incompletely resolved components. Two components are barely resolved in B_2' separated from the two main components of B_1' by 0.0364 ± 0.0005 eV. Line B_3', which has no resolved structure, is 0.0364 ± 0.001 eV below the center of B_2'. The B' lines occur at a slightly lower energy than the series B in Fig. 1. The peak of the B_1' line is 0.0044 eV lower in energy than B_1.

Similar four line spectra have been observed in high-purity ($\mu_n=6500$ cm^2 V^{-1} sec^{-1} at 300°K) GaAs grown by the iodide vapor disproportionation reaction,[15] and in two GaAs crystals ($\mu_n=4500$ cm^2 V^{-1} sec^{-1}, $n\cong3\times10^{16}$ cm^{-3}) pulled from quartz crucibles. It appears that this type of four line spectra may be observed in crystals with reasonably high mobility and carrier concentration less than 10^{17} cm^{-3}.

As the sample temperature is increased above 4.2°K, the emission spectrum of Figs. 1 and 2 decreases in intensity. The lowest energy components of each of the B' lines decrease in intensity more rapidly than the higher energy components of the B' lines. At about 20°K the rate of decrease of the series B and B' becomes very rapid, and by 40°K they are too weak to observe. Only line A remains. In Fig. 2 only the high-energy component of line A is observable above about 10°K. Figure 3 shows line A at 77°K of a typical crystal grown in an O_2 atmosphere. The AlN crystals showed similar spectra except that the line was somewhat broader.

The optical absorption measurements of Sturge[11] clearly show a bump on the absorption edge at an energy ($\sim$1.49 eV) very close to the photon energies of lines B_1 and B_1'. We have made rough measurements of optical absorption on two pulled crystals. One, which was pulled from AlN and exhibits the fluorescence of Fig. 1, clearly has a bump in absorption similar to that observed by Sturge. The second crystal which was pulled from quartz and exhibited only a broad ($\Delta E\cong0.02$ eV) emission band at 1.50 eV showed no bump in optical absorption. It would appear that the emission line B_1, and the absorption bump arise from the same process.

The series of lines B and B' are similar to the edge emission which has been observed in a number of 2–6 compounds,[4] e.g., the green emission in CdS,[16] but has not been previously reported in any 3–5 compounds. It has been interpreted as recombination of an electron with a hole trapped at a center (or vice versa) with the emission of zero, one, and two optical mode phonons.[17] The fact that the lines are wider than kT and that there is structure in the series B' indicates that the center (or centers) does not give rise to a single energy level but to a complex set of levels. Since the emission is observed in GaAs grown by three different methods it is tempting to ascribe it to an intrinsic defect, such as a vacancy or an interstitial gallium or arsenic atom.

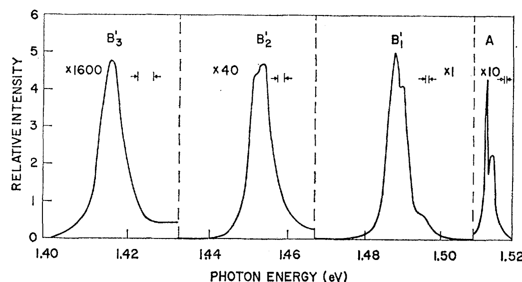

FIG. 2. Typical spectrum of a boat grown crystal in an O_2 atmosphere. The oxygen pressure for this crystal was 155 mm Hg, $T=4.2°K$. (The scale is linear in wavelength.)

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Emission line A occurs at a photon energy of 1.5143 ± 0.0005 eV. (The uncertainty is due to a small variation of the position of the line from sample to sample.) In Fig. 2 it is the high-energy component of line A that occurs at this energy. This energy is very close to the energy of the exciton absorption line, 1.5177 ± 0.0015 eV found by Sturge.[11] The difference is just outside the experimental error and is believed to be due to a questionable correction of the absorption data. Sturge found the absorption constant in the thinnest sample, where the exciton line is observed, does not join continuously onto the absorption constant in thicker samples. He interpreted this as a change of energy gap due to surface damage introduced during the mechanical polishing of the samples. He shifted the exciton absorption energy by 0.005 eV to bring the data in the different samples into coincidence. Similar effects due to surface damage have been observed in other materials: ZnO[18] and ZnTe.[19] In these cases it has been found that at least the major part of the effect of surface damage is to cause a change of absorption constant with no energy gap change. On this basis, at most a much smaller correction to the exciton absorption energy should be made in the absorption data. Sturge's uncorrected value of the exciton absorption is 1.513 eV, which is within experimental error of the photon energy of line A. By fitting the shape of the absorption curve, Sturge finds the exciton binding energy $\epsilon_b = 0.0034$ eV, which is, as expected, less than the binding energy for donors or acceptors ($\cong 0.0082$ eV) on the basis of the effective mass approximation. It would seem then that line A is not due to recombination of electrons and holes via a shallow donor or acceptor state but due to exciton annihilation. Because of the small value of ϵ_b, free-electron-hole recombination may also be contributing to line A, especially at higher temperatures.

It is possible to get some further information on the relative importance of exciton annihilation and free-electron-hole recombination. Figure 4 is a plot of the photon energy of the peak of line A as a function of temperature. The uncorrected photon energy of the peak of the exciton absorption line from Sturge's data is also plotted. It is seen that the two curves are parallel within ± 0.0005 eV over the whole temperature range. If exciton recombination were dominant at low temperatures and free-electron-hole recombination at high temperatures, the curves would diverge with increasing temperature by an amount equal to the exciton binding energy, 0.0034 eV. Therefore, it must be concluded that one process dominates over the whole temperature range.

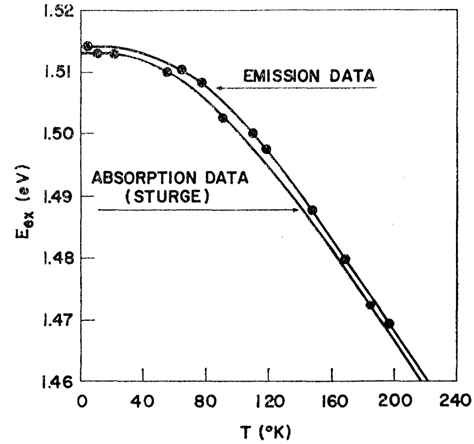

FIG. 4. The photon energy of the peak of line A vs temperature. The exciton line observed in absorption is also plotted.

In order to find out which process dominates we can examine the line shape. From the principle of detailed balance[20] it can be shown for free-electron-hole recombination that the number of photons emitted per unit energy interval is

$$n(\epsilon) \propto \frac{\epsilon^3 \alpha}{\exp(\epsilon/kT)-1}, \tag{1}$$

where ϵ is the photon energy and α is the absorption constant. The energy dependence of the absorption constant for parabolic energy bands is given by[21]

$$\alpha \propto \frac{\exp x}{\epsilon \sinh x}, \quad x = \pi \left(\frac{\epsilon_b}{\epsilon - \epsilon_g} \right)^{1/2}, \tag{2}$$

where ϵ_g is the energy gap and ϵ_b is the exciton binding energy. Sturge finds that his absorption data fit Eq. (2). Using the values found by Sturge for ϵ_b we find line A at 4.2°K is much wider than calculated from Eqs. (1) and (2). At 77°K, on the other hand, the experimental curve is narrower than the calculated one as shown in Fig. 3 (the calculated curve is fitted to experiment at the peak). Hence, line A cannot be due to free-electron-hole recombination. Unfortunately, no theory exists for the exciton absorption line shape for direct semiconductors. Since it is entirely possible that the absorption process does not conserve photon energy, i.e., it may involve

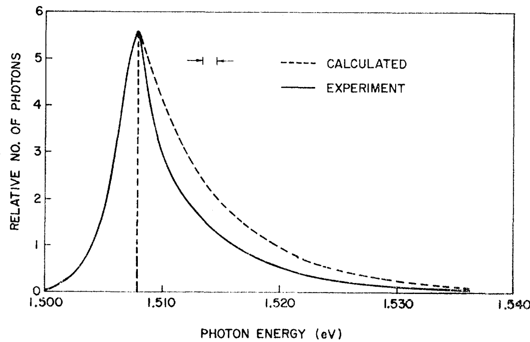

FIG. 3. Typical spectrum at 77°K. Line A is the only one still observable. The calculated curve is computed for free-electron hole recombination.

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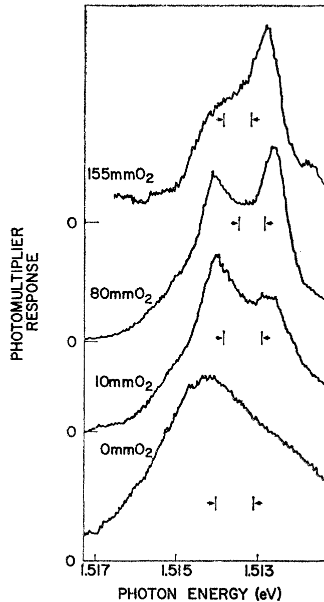

FIG. 5. Tracings of the photomultiplier response for several crystals grown under different O_2 pressures (expressed in mm Hg). The high-energy line is the intrinsic line. The curve labeled 0 mm (Hg) is an AlN pulled crystal, $T=4.2°K$.

phonons, the principle of detailed balance cannot be applied in a simple way to the absorption data on the exciton line. Furthermore, there may be some broadening of the exciton line in Sturge's data due to the surface damage. Indeed it is found that if Eq. (1) is applied to Sturge's data assuming energy conserving transitions the observed emission is too narrow. However, for the reasons stated above this does not mean that the emission is not an exciton line. Since it appears that no other mechanism can give rise to emission lines narrower than kT, it seems reasonable to ascribe line A to direct recombination of excitons. If the emission[1] and absorption[22] data for germanium and silicon are compared, it also is found that the exciton recombination is important over the whole temperature range (up to 300°K).

In Fig. 2 line A is a doublet. The high-energy component is the intrinsic component. The lower energy component, which is sometimes very narrow ($\Delta e \cong 0.0005$ eV), occurs in all crystals grown in an O_2 atmosphere. Moreover, its strength relative to the intrinsic line varies monotonically with O_2 pressure used during growth as shown in Fig. 5. Figure 6 shows the ratio of the O_2-dependent line to the intrinsic line as a function O_2 pressure. The square root law is to be expected from the

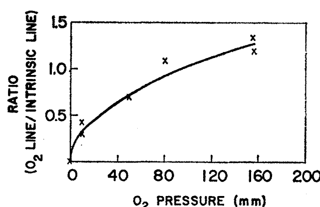

FIG. 6. The points plotted are experimental values of the ratio of the O_2-dependent emission line to the intrinsic line vs O_2 pressure. The curve is the square root of the O_2 pressure.

[22] See T. P. McLean, *Progress in Semiconductors* (John Wiley & Sons, Inc., New York, 1960), Vol. 5, p. 53 and the original references quoted there.

mass action law if the oxygen goes into the lattice as a neutral impurity atom.

The O_2-dependent line appears to be similar in origin to what has been observed in other semiconductors.[1–3,23] It is attributed to annihilation of an exciton bound to an impurity center (probably oxygen). In some crystals grown in high (155 mm Hg) O_2 pressure a weak emission line is observed, 0.0016 eV above the intrinsic exciton line. The origin of this line is not understood.

In the crystals which were grown at a low pressure of O_2 (10 mm of Hg), an emission line at 1.389 eV was also observed with a phonon satellite 0.036 eV below it.

Emission was also observed from GaAs crystals doped with Zn, Cd, Te, and Sn and also from undoped crystals pulled from quartz crucibles. Typical spectra in the vicinity of the absorption edge are shown in Fig. 7. A simple broad line, somewhat below the energy gap in pure material, is observed. The position of the line varied with the doping element between 1.44 and 1.51

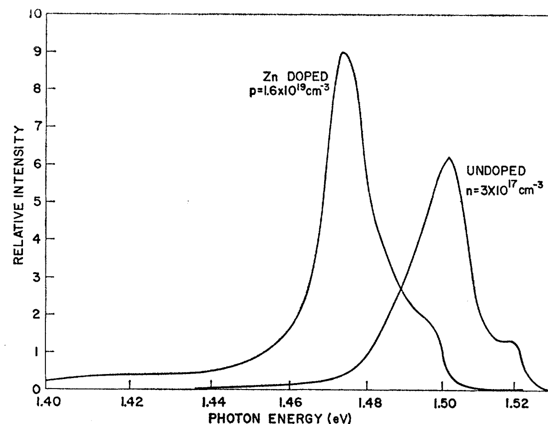

FIG. 7. Typical emission spectra of impure crystals, $T=4.2°K$.

eV. A broad band at 0.95 eV similar to that observed by Pankove and Massoulie[9] has also been seen in some crystals.

Note added in proof. More extensive fluorescence measurements of homogeneously doped samples of GaAs have been made. A comparison of fluorescence measurements of Te and Zn doped samples with the emission from forward biased diodes at 77°K in the region of the absorption edge have been published [M. Nathan and G. Burns, Appl. Phys. Letters **1**, 89 (1962)].

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