VII-6.

Cathodoluminescence of *p*-Type GaAs

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Zn-doped GaAs specimens with carrier concentrations from 3×10^{16} to 1.2×10^{20} cm⁻³ were bombarded with 24 kV electrons. The emission spectra show the evolution of the acceptor band and its merger with the valence band tail as the Zn concentration increases.

It appears that the emission results from donor-to-acceptor transitions, the donors forming a narrow band of states.

§1. Introduction

The primary objective of this work was to study the emission spectrum from bulk GaAs as a function of doping and to infer from this data the effect of impurities on the density of states in the semiconductor. Emission from electroluminescent *p-n* junctions has been used to assess the distribution of states in the gap and to identify the transport mechanism responsible for luminescence.¹⁻⁷⁾ However, the specific influence of doping on the band structure is masked by the fact that not only donors and acceptors are present but also their concentrations vary through the junction. Some information has already been gained by absorption measurements in uniformly doped bulk GaAs.⁸⁾ However, in *p*-type GaAs, the absorption process connects only the filled states below the Fermi level to empty states in the conduction band. Therefore, although one gains insight into the effect of acceptors on the conduction band, very little can be inferred about the distribution of acceptor states which are mostly above the Fermi level. Emission in ptype material, on the other hand, involves states lying above the Fermi level and thus yields information related to the distribution of states in the acceptor band and in the tail of the valence band. Such measurements have already been reported by Cusano⁹⁾ and data is also available from photoluminescence.^{10,11)} In the present work, the same material which had previously been studied by absorption⁸⁾ was re-examined by cathodoluminescence and some additional samples were tested as well. The resulting data reveals new features which will be discussed in the last section.

§2. Experimental

The specimen consisted of a small parallelepiped mounted on the cold finger of a cryostat. The emission was observed from a facet perpendicular to the bombarded surface.

A 21 to 24 kV beam was used. The maximum current was 3 mA, which corresponds to a current density of the order of 4.5 A/cm^2 . The excitation consisted of a burst of pulses gated by a synchronous amplifier. The pulse duration and repetition rate could be controlled (70 nsec minimum pulse length). The amplified output of the detector could be recorded either linearly or logarithmically to assist further processing of the data.

§ 3. Results

Typical emission spectra at 4.2° K for four different zinc concentrations are shown in Fig. 1.



Fig. 1. Emission spectra of Zn-doped GaAs at 4.2°K.

As the zinc concentration is increased;

1. The emission peak shifts from 30 meV below the energy gap of pure GaAs to still lower energies;

2. The bandwidth increases;

3. The high energy edge exhibits an abrupt cut-off when the carrier concentration is greater than about $6 \times 10^{18} \text{ cm}^{-3}$;

4. An extensive low energy tail develops at high concentrations.

5. The low energy tail of many samples shows a bump some 35 to 40 meV below the main peak.

In some cases three such bumps attributed to L. O. phonons can be found about 40 meV apart.

6. The energy and shape of the emission peak remain nearly constant as its intensity is varied over three to four orders of magnitude.

The position of the emission peak as a function of doping is shown in Fig. 2. The 3×10^{16} cm⁻³ sample exhibited three peaks: the most intense at 1.484 eV attributed to donor-acceptor transitions, another peak at 1.500 eV of unknown origin and a smaller peak at 1.449 eV probably due to a transition with LO phonon emission. Cusano's data⁹⁾ obtained at 20°K has also been included. The two sets of data are in close agreement. Figure 2 shows that the emission peak begins shifting by at least 50 meV when the concentration exceeds 10^{20} cm⁻³. This shift goes roughly as the 2/3 power of the hole concentration.

Figure 2 shows also the energy E_f at which the high energy edge cuts off. E_f is attributed to the position of the Fermi level in the valence



Fig. 2. Concentration dependences of emission peak and of high energy cut-off.



Fig. 3. Concentration dependence of emission linewidth.

band, forming, at low temperature, a sharp demarcation between allowed and forbidden transitions. This cut-off becomes more gradual and then disappears when the sample is warmed up. Numerically, E_f was chosen as that point of the spectrum which is 3 db below the high-energy knee. This quantity relates to the Burstein shift.

The linewidth, plotted on Fig. 3, shows the rapid widening of the acceptor band as the impurity concentration goes through the 10^{19} to 10^{20} range.

A logarithmic recording of the emission spectrum is shown in Fig. 4. The emission spectrum consists of three main regions each of which seems to have an exponential dependence on energy of the form $L = L_0 \exp(h\nu/E_n)$. Hence a logarithmic plot of the emission spectrum consists of straight lines as shown in the inset of The reciprocal slopes are E_1 for the Fig. 5. high energy edge and E_2 for the low energy edge of the main emission band. Below this band, one finds the low energy tail of reciprocal slope Note that at high doping, the edge E_1 E_3 . breaks steeply at the high energy knee E_f . The concentration dependences of the three coefficients E_1 , E_2 , and E_3 are shown in Fig. 5.



Fig. 4. Logarithmic recording of emission spectrum (4.2°K).



Fig. 5. Concentration dependences of parameters characterizing spectral shape.

Although all three coefficients have a strong concentration dependence above 10^{19} cm^{-3} , E_1 is the most sensitive parameter, being approximately proportional to the hole concentration.

§4. Discussion

The energy of the emission peak does not shift appreciably when the beam current is varied over a large range corresponding to a large shift of quasi-Fermi levels. Assuming a carrier lifetime of 10⁻⁹ sec.,¹²⁾ a threshold of 4.5 eV for pair formation by electron bombardment¹³⁾ and a penetration depth of 1μ , the carrier density generated by a 24 kV beam at a current density of 4.5 A/cm² is 1.5×10^{18} carriers/cm³. This corresponds to an electron quasi-Fermi level of 67 meV. Therefore, if the emission were due to transitions from the conduction band to the valence band or from the conduction band to empty acceptor states, a considerable shift of the emission spectrum would obtain upon changing the beam current by several orders of magnitude. This absence of emission shift can be explained by a much stronger coupling for radiative transitions between donors and acceptors than for

transitions between conduction band and either acceptors or valence band. Furthermore, it is required that the donors form a narrow band of states, at most 4 meV wide, the maximum shift observed. When the quasi-Fermi level for electrons is above the donor states the electrons return radiatively to the valence band by a donor-to-acceptor transition, the only detectable radiative transition. In absorption measurements, the acceptor-to-donor transition is not detectable at low temperatures because most of the acceptor states are empty of electrons.

Now we can try to assess the average donor and acceptor binding energies: their sum $(E_A + E_D)$ is given by the difference between the energy gap (assumed constant) and the energy of the emission peak $(1.515 - h\nu_p)$. This quantity is plotted in Fig. 6a. It shows that in the least heavily doped materials $E_A + E_D = 30$ meV. As the acceptor concentration increases above $6 \times$ 10^{18} cm^{-3} , the emission peak shifts as the 2/3 power of the concentration (Fig. 6b). Since the acceptor binding energy decreases with increasing concentration,¹⁴⁾ this shift may reflect the formation of a tail of states as the edge of the valence band: as the density of acceptors increases, their distribution spreads over a larger



Fig. 6. Concentration dependence of: (a) $1515 - h\nu_p$ in meV, (b) $1515 - h\nu_p - 30$.



Fig. 7. Concentration dependence of $E_f - h_{\nu p}$ compared to theoretical Burstein shift and to Burstein shift from absorption data.

range of energies and shifts closer to the center of the energy gap.

A plot $E_f - h\nu_p$ as a function of carrier concentration (Fig. 7) yields the surprising result that this energy difference varies as the 2/3 power of the carrier concentration. This dependence may be no more than an intriguing coincidence. However, there is a striking similarity between this representation of the Fermi level shift with concentration and the Burstein shift calculated on the basis of an unperturbed parabolic band (Fig. 7). The absorption data⁸⁾ shown in Fig. 6 is the result of an extrapolation which assumed the valence band to be parabolic at the Fermi level.

Let us consider now the high energy knee of the emission spectrum (Fig. 4). The high energy edge of the acceptor band component can be extrapolated towards the cut-off E_f . The difference between the actual curve and the extrapolation represents the density of empty states in the valence band (or in its tail). A greatly expanded recording of this knee was used to extract this quantity. Its value is plotted in Fig. 8. From this plot one concludes that the



Fig. 8. Evaluation of distribution of valence band states from data of Fig. 4.

density of states in the valence band tail near the Fermi level fits a linear distribution (much better than a quadratic distribution). However, not enough data is available to generalize conclusions about the shape of the valence band tail.

This study suggests that the bias dependent spectral shift in injection electroluminescent diodes, in the range associated with band filling, may represent a filling of the valence band tail rather than a filling of conduction band tails, since in the p-type region the donors seem to form a very narrow band of states.

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