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VII-5. Edge Absorption and Photoluminescence in Disordered Gallium Arsenide

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The optical properties of a range of *n* and *p*-type gallium arsenide samples have been measured for photon energies near to the band gap. The measurements have been made both before and after neutron irradiation to determine the band tailing effects produced by the disorder. Exponential absorption tails were found which were independent of the starting *n*-type samples. Photoluminescence spectra were severely quenched both by neutron and electron irradiation probably due to recombination centres rather than band tailing effects.

§ 1. Introduction

Recent theoretical work[1,2] has shown that a disordered structure may have energy regions of non-localized electron wave functions separated by regions of localized states which may in turn be separated by a forbidden energy gap. The localized states occur near the band edges of the perfect structure and lead to tails on the densities of states on the bands of the perfect crystal. The effects of these tails on optical properties for photon energies close to the band gap in the perfect crystal are expected to be considerable.

The theoretical result depends on the introduction of a randomness into the periodic lattice potential and not primarily on the source of the random potential. It has been applied to disorder arising from high impurity concentrations in semiconductors and to the disorder in liquid semiconductors. The method should be equally applicable to the disorder introduced by heavy particle irradiation - in particular by fast neutron irradiation.

In this case the primary knock-on atoms have high energies ($\sim 10^5$ eV) and can produce large disordered regions in addition to the simpler lattice defects. Fast electron irradiation, on the other hand, will produce only point defects and simple point defect aggregates, including simple aggregates of lattice defects and impurities.

We have measured the absorption edge and the photoluminescence spectra near the edge in a range of gallium arsenide samples. Some optical measurements of neutron irradiated gallium arsenide were reported by Aukerman *et al.*[3] and measurements of the effects of electron irradiation on the cathodoluminescence have been briefly reported by Compton *et al.*[4] and by Loferski and Wu.[5] Loferski and Wu found that the cathodoluminescence excited at room temperature was unaffected by electron bombardment with energies less than 0.280 MeV but considerably quenched by doses of ca. $10^{15}\,e^-\,\mathrm{cm}^{-2}$ at higher energies. These effects presumably arise from the introduction of defect recombination centres and would be expected to occur in neutron irradiations in addition to band tailing effects. We have, therefore, also carried out fast electron irradiations on similar specimens.

§ 2. Specimens and Experimental Conditions

The electrical and optical characteristics of the specimens before irradiation are summarized in Table I. The samples ranged from *n*-type having a carrier concentration at room temperature (n_0) of $3.0\times10^{18}\,\mathrm{cm}^{-3}$ to *p*-type having (p_0) 7.8×10^{17} holes cm^{-3}. A number of specimens were prepared from immediately adjacent parts of each crystal. Specimens were irradiated with a dose of $4.3\times10^{16}\,n^\circ\,\mathrm{cm}^{-2}$ (Ni scale-average neutron energy ca. 1 MeV) at 30°C. Fast (2 MeV) electron irradiations were carried out at room temperature at a flux of 0.5 μA cm^{-2} to a dose of $3.6\times10^{16}\,e^-\,\mathrm{cm}^{-2}$.

Absorption measurements were made at room temperature in a UNICAM SP. 700 spectrophotometer. Luminescence was excited both at 80°K and 300°K by the 5461 and 5780 Å lines of a high pressure mercury lamp. To minimize the self-absorption of the emitted light (lower energy) the emission was studied from the same face of the crystal as illuminated with the exciting light. The exciting light was filtered with $CuSO_4$ and a Chance ORI (removing scattered excited light) filter was used between the analysing monochromator (f/4.5) and the Mullard CVP

Table I. Summary of characteristics of specimens.

Sample types and number	Deliberate dopant	R.T. carrier concentration cm^{-3}	R.T. carrier mobility cm^2/volt/sec.	Emission peaks (eV)		
N1	Te	3.0×10^{18}	2500	1.53	—	1.28
N2	—	2.6×10^{16}	5480	1.49	1.33	—
N3	Compensated semi-insulating	4.5×10^{7}	2300	—	1.35*	—
N4	—	1.5×10^{17}	2400	1.50	(1.41*, 1.36*)	1.24
P5	Zn	1.0×10^{19}	84	1.46	—	—
P6	Zn	7.8×10^{17}	150	1.48	1.35	—

(* emission weak)

150 photomultiplier which was cooled to liquid nitrogen temperature. The emitted light was chopped at 750 c/s and the photomultiplier signal was recorded after passing through a phase sensitive amplifier.

Photoluminescence measurements were carried out with the specimen mounted on a liquid nitrogen cooled copper cold finger in vacuum as well as with the specimen at room temperature. In all emission measurements an unirradiated monitor specimen of the same impurity content was measured with the experimental sample, both before and after the irradiation of the latter. In this way we were able to establish that there was no significant change in the response of the apparatus.

§ 3. Results

Absorption: *n-type*

These results are shown in Fig. 1. After irradiation the absorption spectra of specimens N 2, 3 and 4 were, within the limits of error, identical between 0.50 and 1.25 eV. Furthermore in this region of absorption tail the spectra were exponential with the absorption coefficient (μ cm^{-1}) given by:

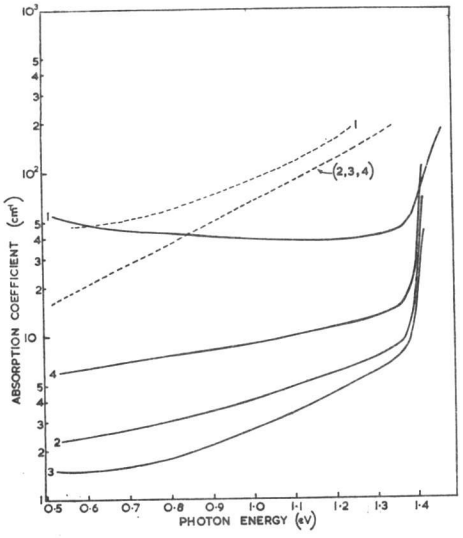

Fig. 1. The absorption spectra of neutron irradiated *n*-type gallium arsenide.

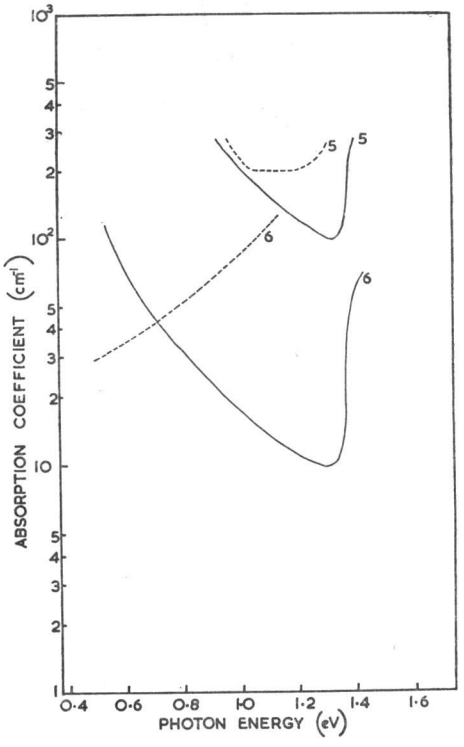

Fig. 2. The absorption spectra of neutron irradiated *p*-type gallium arsenide.

$$\mu = Ae^{B \cdot h\nu},$$

with $B = 3.0 \pm 0.05\ (\text{eV})^{-1}$. At 1.12 eV the absorption coefficients were 90 cm^{-1} for specimens N 2, 3 and 4. The degenerate N 1 showed some impurity or free carrier absorption before irradiation at the lower photon energies. The difference between the absorption spectra of this specimen before and after irradiation in the spectral region away from the stronger free carrier absorption showed an exponential dependence on energy similar to that found for the other specimens. For all *n*-type specimens $\Delta\mu$ at 1.12 eV was $83 \pm 3\ \text{cm}^{-1}$ (*i.e.* $A = 2.82\ \text{cm}^{-1}$).

Absorption: p-type

Both *p*-type specimens (P 5, 6) showed strong free carrier absorption before irradiation. At a photon energy of 0.99 eV the results arose predominately from free carrier effects in both specimens and the absorption ratio (P 5 : P 6) is 12.0 which is in good agreement with the measured free carrier ratio of 12.8.

After irradiation extra absorption is introduced, increasing towards the absorption edge, and the free carrier absorption is reduced. It is difficult to disentangle these two effects but for an appreciable region of the spectrum in P 6 the form approaches the exponential found for the *n*-type samples with $\Delta\mu \sim 10^2$ at 1.12 eV.

For specimen P 6 an estimate of the decrease in carrier concentration produced by the irradiation can be made. At 0.556 eV the absorption ratio before and after irradiation is $\simeq 40$. We expect, therefore, that the carrier concentration has been reduced to at least $1.95 \times 10^{16}\ \text{cm}^{-3}$ giving a carrier removal rate of $(7.80 - 0.195) \times$

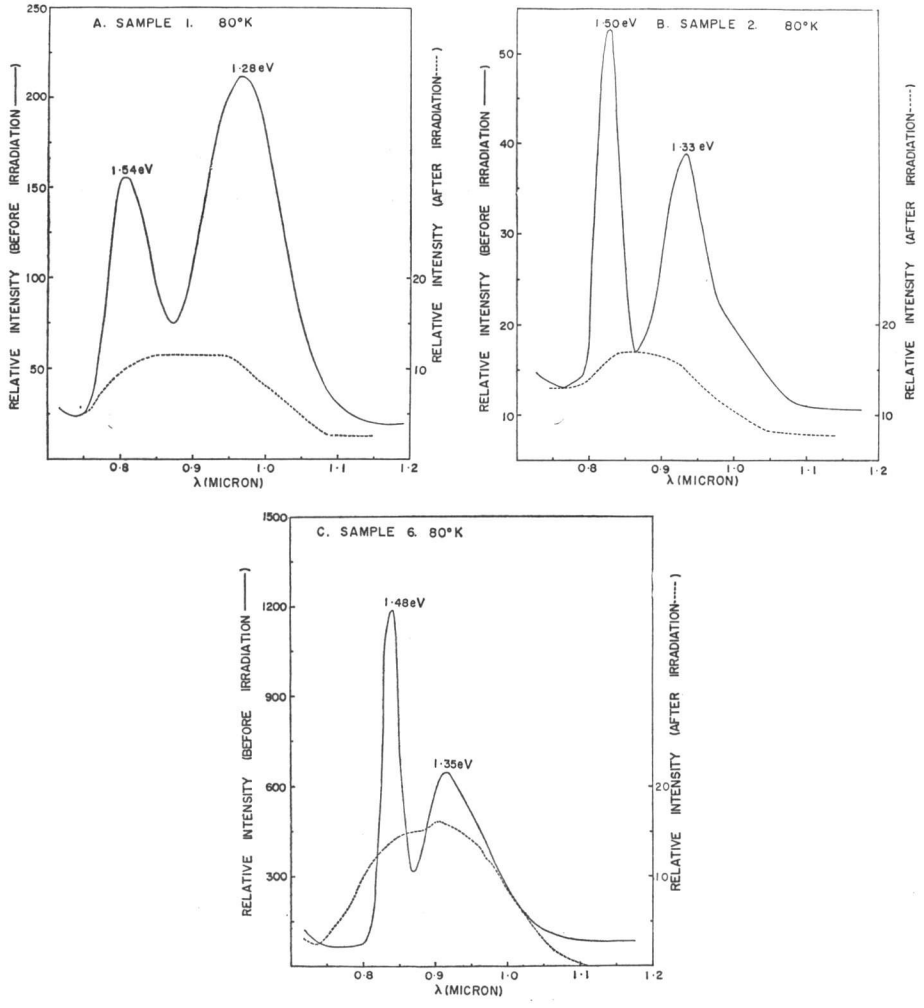

Fig. 3. The quenching of photoluminescence at 80°K in neutron irradiated gallium arsenide: A. Sample N1; B. Sample N2; C. Sample P6.

10^{17} per 4.3×10^{16} $n°$ cm^{-2} which gives, independently of the precise value after irradiation, a rate of 17.7 carriers cm^{-3}/fast $n°$ cm^{-2}.

The quenching of photoluminescence

Before irradiation the following groups of emission peaks were found at 80°K:

Table II. Quenching of photoluminescence by irradiation.
(I_0 intensity before irradiation, I_R after irradiation, $\Delta=I_0-I_R$;
I_0 ane I_0* not same relative scale)

Sample types and number	Peak position (eV)	$n°$ Irradiation			e^- Irradiation		
		I_0	I_R	Δ/I_0	I_0*	I_R*	Δ*/I_0
N1	1.53 1.28	155 211	10 10	0.93 0.95	4.77 5.70	0.64 1.30	0.87 0.77
N2	1.49 1.33	52.8 38.8	16 15.8	0.68 0.59	— —	— —	— —
N3	1.35	85.2	15	0.82	—	—	—
N4	1.50 1.24	31.6 38	15 12	0.53 0.68	— —	— —	— —
P5	1.46	371	19	0.95	9.05	0.80	0.91
P6	1.48 1.35	1188 645	15 16	0.99 0.97	8.40 6.36	0.83 3.32	0.91 0.48

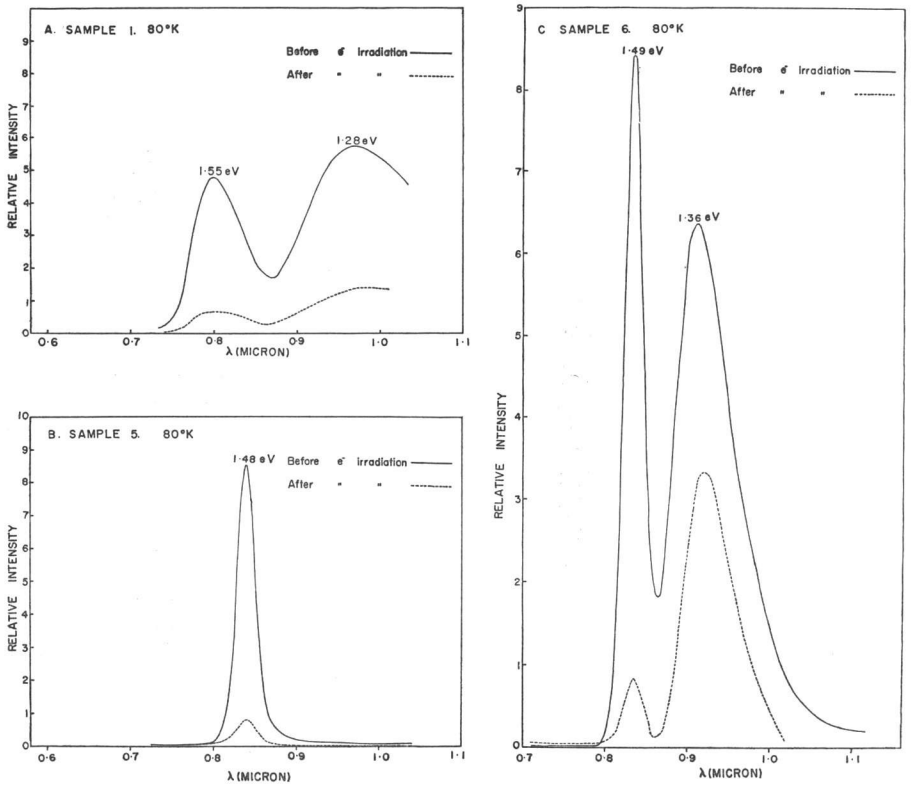

Fig. 4. The quenching of photoluminescence at 80°K in electron irradiated gallium arsenide:
A. Sample N1; B. Sample N2; C. Sample P6.

A. 1.46–1.53 eV; B. 1.33–1.36 eV; and C. 1.24–1.25 eV. There is doubt as to which groups 1.2 (N 1) and 1.41 (N 4) should be allotted. The variation in peak position of the edge emission (A) most likely arises from the variation of the absorption edge shape in that region, as discussed by Lucovsky *et al.*[5]. The variations in the other cases are more likely to arise from the experimental conditions.

In the semi-insulating specimen the A peak was absent. It appears, therefore, that the deep impurity traps which produces the low carrier concentration in semi-insulating material also provide efficient recombination centres for holes and electrons. The relative persistence of a low energy peak in the semi-insulating sample could be accounted for by assuming that each of those transitions occurred in single impurity centres. In contrast the edge emission if it were either exciton emission, donor to band or band to acceptor (all involving extended wave functions to some extent) would be more effectively quenched by recombination centres.

All emission peaks were quenched by the neutron irradiation. The slits had to be opened to record the after irradiation spectra so that the relative values after irradiation are not completely reliable. However, we define $(I_0-I_R)/I_0$ as a measure of the completeness of the quenching and the exact value of the intensity after irradiation (I_R) is not important in these cases where it is low. The results are summarized in Table II.

The effect of 2 MeV electron irradiation has been studied for N 1, P 5 and P 6. Considerable quenching occurs as may be seen from Fig. 4. and Table II.

§ 4. Discussion of Results

The results show that, more or less independently of the starting *n*-type material, the same exponential tail to the absorption edge in obtained after the neutron irradiation. The effects of band tailing produced by disorder in *p*-type are more difficult to separate because of the initial strong free carrier absorption. However, there was evidence that a similar tail was present after irradiation in P 6.

The constancy of the effects in the various *n*-type samples indicate that the band tailing is probably a disorder phenomenon, the same degree of disorder being produced in all the samples. It should be possible to determine the pair correlation function for such irradiated materials by long wavelength neutron scattering and make a more quantitative comparison with the band theory of a disordered lattice.

The exponential dependence of the absorption coefficient on photon energy is consistent with the occurrence of exponential tails on the densities of states.

As may be seen from Table II there are large decreases in photoluminescence brought about by electron and neutron irradiation. It is clear that $3.6\times10^{16}\,e^-\,\mathrm{cm}^{-2}$ are not as effective in reducing the emission intensity as $4.3\times10^{16}\,n^\circ\,\mathrm{cm}^{-2}$. If both effects were in a linear dose region the e^-/n° ratio for identical effects would be ca. 1.4 (P 5) and 6.6 (P 6). In the absence of dose curves we are not sure how close these values are to the true ratio of the cross-section for displacements $\sigma_d(n^\circ)/\sigma_d(e^-)$ although we note that from the carrier removal rate in P 6 we can estimate a e^-/n° ratio of about 3.

Acknowledgement

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References

1) A. I. Gubanov: *Quantum Electron Theory of Amorphous Conductors* Chp. 4 (1963): (Translation, New York, Consultants Bureau, 1965).
2) L. Banyai: *Proc. Int. Conf. Semiconductor Physics* Paris, (1964) p. 417.
3) L. W. Aukerman, P. W. Davis, R. D. Graft and T. S. Shilliday: J. appl. Phys. **34** (1963) 3590.
4) D. M. J. Compton, G. T. Cheney and J. F. Bryant: *Proc. Int. Conf. Semiconductor Physics*, Paris (1964) p. 235.
5) J. J. Loferski and M. H. Wu: *Proc. Int. Conf. Semiconductor Physics*, Paris (1964) p. 212.
6) G. Lucovsky, A. J. Varga and R. F. Schwartz: Solid State Commun. **3** (1965) 9.

DISCUSSION

Urli, N.B.: We have obtained similar results in the case of *p*-type CdTe after thermal- and fast-neutron irradiation. Optical absorption and thermally-stimulated-current measurements indicate the existence of quasi-localized levels which extend quite deeply in the forbidden gap.

Bonch-Bruevich, V. L.: There is no direct explicit relation between the form of the density of states tail and the tail experimentally observed in the absorption coefficient. There is however a correlation between the two tails. So the very interesting results reported by Prof. Mitchell do show rather definitely that there is a density of states tail but do not make it possible to draw definite conclusions as to the form of this tail. In this respect, I should like to remark that it might be more convenient to study not the band-to-band but the band-to-impurity transitions. It has been shown by Drugova and myself that in this case there are conditions under which the form of the absorption coefficient does reproduce the density of states tail.

Mitchell, E. W. J.: In optical work one has to deal with product of densities of states and transition probabilities and I agree that it is not possible to extract densities of states tail from the data without some assumption about the transition probabilities.

Redfield, D.: Have you studied any photoconductivity or impurity band conduction in such samples ?

Mitchell, E. W. J.: Not yet. We plan to make photoconductivity measurement to try to distinguish the localized and non-localized states which I mentioned.

Ito, K.: How is the degree of disorder of your specimens ?

Mitchell, E. W. J.: The whole of the specimen was not disordered. The concentration of disordered material in our samples might be of order $10^{-2}\%$.