

## Minority Carrier Diffusion Lengths for High Purity Liquid Phase Epitaxial GaAs

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### *Abstract*

Measurements of minority carrier diffusion lengths for p-type and n-type GaAs were carried out using an electron beam induced current (EBIC) technique. The GaAs material was grown by liquid phase epitaxy (LPE) at the Australian Nuclear Science and Technology Organisation. The diffusion lengths measured for high purity p-type and n-type LPE-GaAs samples were observed to be longer than any previously reported.

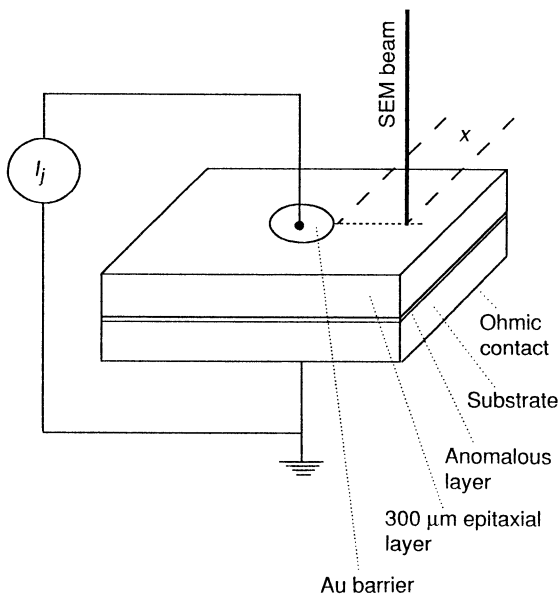
### 1. Introduction

The diffusion length of minority carriers  $L_{p,n}$  is an important characterisation parameter in semiconductor materials and is of particular interest when constructing devices such as solar cells (Hovel 1975), double heterojunction lasers (Casey and Panish 1978) and bipolar transistors. Their efficiency depends primarily on the ability of minority carriers to diffuse through neutral material to a p–n junction or Schottky barrier where they recombine with majority carriers. For this reason diffusion lengths have been measured in a variety of semiconductor materials.

The liquid phase epitaxial (LPE) GaAs examined here was grown for possible construction of room temperature semiconductor detectors of X-rays and soft  $\gamma$ -rays (Alexiev and Butcher 1992). For these devices a Schottky barrier is constructed on a 100–300  $\mu\text{m}$  thick GaAs epitaxy; the depletion region formed by the Schottky barrier is the detector's sensitive region since majority carriers, created as electron–hole pairs during the impact ionisation initiated by incoming photons, are collected with high efficiencies in this region of the detector.

The reason for measuring  $L_{p,n}$  in these majority carrier devices was to confirm the quality of the material grown. Low carrier concentrations are required for the formation of a depletion region of adequate depth for the detection of penetrating radiation, but freedom from carrier recombination centres is a further requirement since this improves energy resolutions and charge collection properties. Radiation detectors made so far from the LPE material have shown good energy resolution, qualitatively indicating high purity material (Alexiev and Butcher 1992). Also, deep level transient spectroscopy (DLTS) measurements have shown no detectable deep level recombination centres (Alexiev 1990)—again indicating high purity material. The  $L_{p,n}$  measurements can establish semiconductor purity because

the presence of recombination centres within an epitaxial layer will result in reduced values of  $L_{p,n}$ . These centres are associated with a variety of defects and impurities in the material, including Ga vacancies (Ettenberg *et al.* 1976) and residual impurities such as oxygen and transition metals as reported by Jastrzebski *et al.* (1979). However, of particular concern are large concentrations of non-radiative recombination centres in the melt-grown substrate (Sekela *et al.* 1975) which are used for the growth of the epitaxial layers. Jastrzebski *et al.* (1979) reported that under particular conditions, influenced by growth parameters and growth mode, out-diffusion may occur from the substrate into the epitaxial layer. For this reason  $L_{p,n}$  is of immediate interest as a means of assessing the quality of an epitaxial layer.



**Fig. 1.** Schematic of GaAs sample showing the electron beam path and the current measurement path.

## 2. Measurement of $L_{p,n}$

The measurement of  $L_{p,n}$  using electron beam induced currents (EBIC) is based on work by Higuchi and Tamura (1965) and Wittry and Kyser (1965) who found  $L_{p,n}$  values for p-n junctions. A recent review of EBIC methodology using scanning electron microscopes (SEM) was given by Holt (1989), though the method used here was first suggested by Thornton (1968). Briefly, an electron beam incident normal to a Schottky diode is slowly scanned across the surface of the sample. No bias is applied to the diode and the short circuit current induced by the electron beam is measured as a function of the distance  $x$  between the beam and the edge of the surface diode, as shown in Fig. 1.

When the electron beam penetrates a specific distance into the epitaxial layer, a point source of excess electrons and holes is established; these then diffuse through the zero-field region of the epitaxy. If the material is n-type, holes reaching the zero-bias depletion region under the Schottky contact are rapidly collected; if the epitaxy is p-type then the opposite applies, with electrons being collected.

It is more usual for p-n junctions or Schottky barriers to have the electron beam scanned parallel to the junction, as described by Leitch *et al.* (1981); the resulting current  $I_j$  varies with distance  $x$  from the Au barrier as

$$I_j \propto \exp(-x/L_{p,n}). \quad (1)$$

Ioannou and Dimitriadis (1982) have examined the alternative case of scanning the beam normal to the plane of the Schottky barrier. They found that in the presence of an infinite surface recombination velocity  $S$ ,  $I_j$  obeys the relation

$$I_j \propto x^{-3/2} \exp(-x/L_{p,n}). \quad (2)$$

Kuiken and van Opdorp (1985) extended this treatment to include the effect of finite values of  $S$ . However, both those reports assumed a zero-bias barrier depletion width much smaller than the depth of the point source of minority carriers generated in the semiconductor by the electron beam. This approximation did not hold for the low carrier concentration samples studied here since they had zero-bias depletion regions of the order of the depth of the point source. The large depletion regions provided a charge collection plane parallel to the electron beam in a geometry which approaches that of a p-n junction held parallel to an electron beam. It is therefore reasonable to expect a situation where  $I_j$  is described by equation (1) at least to a first-order approximation. Thus if a straight line results from a plot of  $\ln|I_j|$  versus  $x$ , then the slope will equal  $-1/L_{p,n}$ . Corresponding values of  $\tau_{p,n}$  will be given by

$$\tau_{p,n} = L_{p,n}^2/D_{p,n}, \quad (3)$$

where  $\tau_{p,n}$  is the carrier lifetime,  $D_{p,n}$  is the hole or electron diffusion coefficient  $[(kT/q)\mu_{p,n}]$ , and  $\mu_{p,n}$  is the hole or electron mobility.

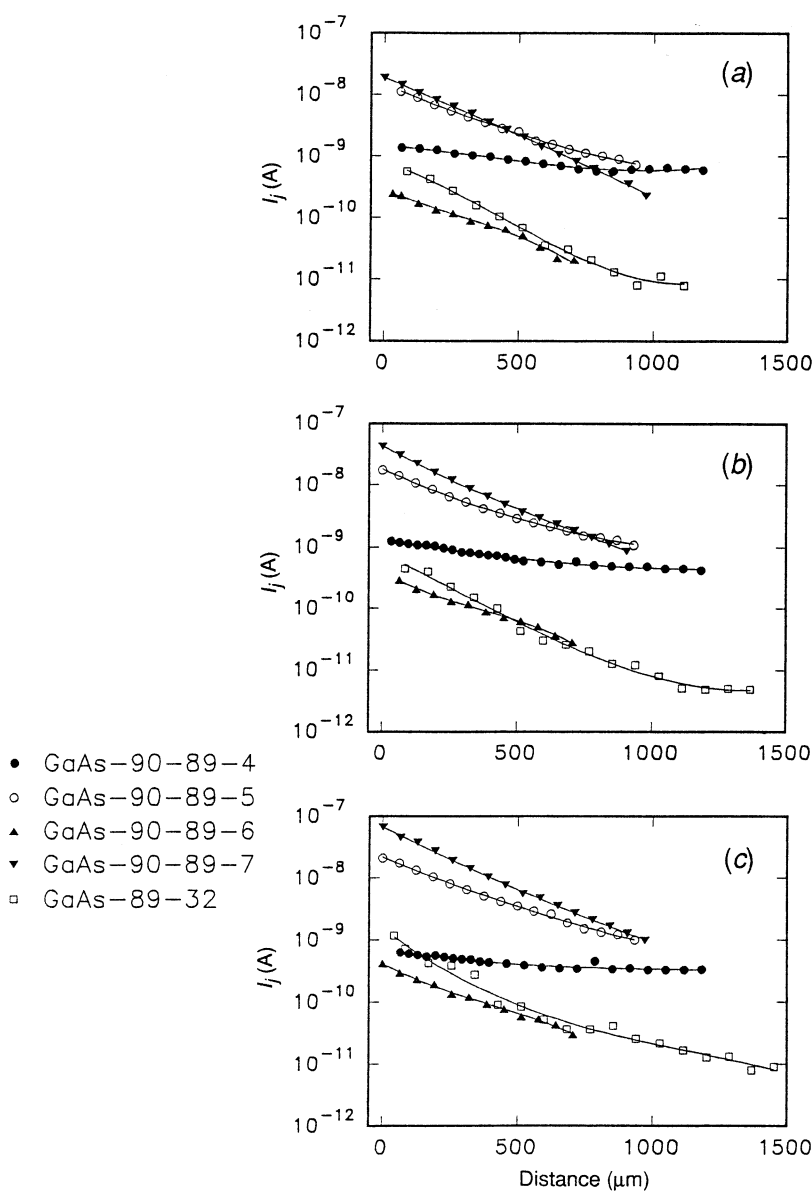
### 3. Experimental

Sample preparation followed standard procedures: a chemically cleaned section of LPE-GaAs is etched, masked and a 2 mm diameter Au area on the epitaxy and an Al surface on the substrate are evaporated to form the surface barrier and ohmic contact respectively.

The SEM used for these experiments was a JEOL JXA840. The beam distance from the Au barrier was calibrated by simply photographing the sample and relating its magnification bar (in  $\mu\text{m}$ ) to the beam position on the screen of the SEM system. Particular attention had to be paid to shielding the internal signal lead from stray current pickup due to secondary electron scattering. The diode (surface barrier) circuit was earthed at one point only; the current measuring instrument, a Keithley 614 electrometer, was left floating (see Fig. 1).

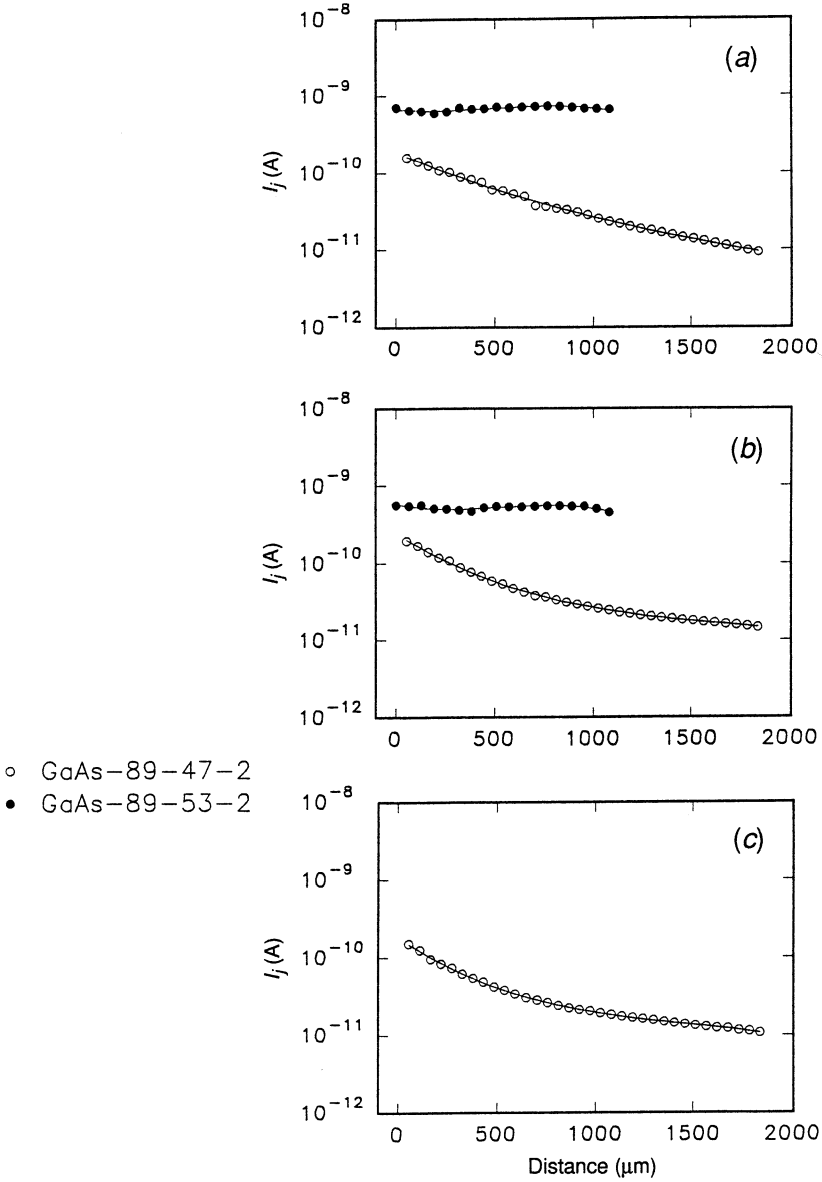
### 4. Results

A number of p- and n-type LPE-GaAs samples of various net carrier concentrations were examined at different beam voltages. EBIC versus distance plots, measured at 300 K, are shown in Figs 2 and 3. For all but one of the



**Fig. 2.** Measured EBIC currents for n-type GaAs samples using different electron beam voltages: (a) 15 kV, (b) 25 kV and (c) 35 kV.

samples (GaAs-89-53-2) the initial decrease in the current  $I_j$  closely followed equation (1), but was then followed by a slower decrease at larger distances, apparently representing a second diffusion length  $L_2$  notably longer than the first. Such changes in slope for GaAs samples have also been noted by Ryan and Eberhardt (1972) and Wittry and Kyser (1965). The processes determining currents at larger distances from the barrier (or p-n diffused junction) were



**Fig. 3.** Measured EBIC currents for p-type GaAs samples using different electron beam voltages: (a) 15 kV, (b) 25 kV and (c) 35 kV.

tentatively explained by Wittry and Kyser (1965) as being the result of majority carrier production by infrared radiation absorbed near the Schottky barrier. This phenomenon was originally predicted by Dumke (1957). Holt and Chase (1973) confirmed the explanation of Wittry and Kyser (1965) and have further found that the value of  $L_2$  is dependent on  $x$ ; so that at  $x = 1000 \mu\text{m}$ , for instance, the observed value of  $L_2$  would be  $\sim 1000 \mu\text{m}$ .

**Table 1.** Measured and theoretical values of minority carrier diffusion length  $L_p$  and lifetime  $\tau$  for n-type GaAs

Specimen	$N$ ( $\text{cm}^{-3}$ )	Theoretical values		Measured $L_p$ ( $\mu\text{m}$ )		
		$L_{\text{dr}}$ ( $\mu\text{m}$ )	$\tau_{\text{dr}}$ ( $\mu\text{s}$ )	15 kV	25 kV	35 kV
GaAs-90-89-4	$1 \times 10^{13}$	770	600	830	780	920
GaAs-90-89-5	$2 \times 10^{14}$	174	29	270	260	260
GaAs-90-89-6	$1 \times 10^{14}$	250	62	270	280	280
GaAs-90-89-7	$1.4 \times 10^{14}$	208	42	230	210	200
Ryan & Eberhardt	$6 \times 10^{13}$	320	100	100	200	200
Alferov <i>et al.</i>	$5 \times 10^{15}$	34	1.1		11.1	
Wittry & Kyser	$5.1 \times 10^{16}$	10	0.1		4	
Tansley	$2 \times 10^{18}$	1.8	0.003		1.6	
Hwang	$2 \times 10^{16}$	18	0.3		1.5	

**Table 2.** Measured and theoretical values of minority carrier diffusion length  $L_n$  and lifetime  $\tau$  for p-type GaAs

Specimen	$N$ ( $\text{cm}^{-3}$ )	Theoretical values		Measured $L_n$ ( $\mu\text{m}$ )		
		$L_{\text{dr}}$ ( $\mu\text{m}$ )	$\tau_{\text{dr}}$ ( $\mu\text{s}$ )	15 kV	25 kV	35 kV
GaAs-89-53-2	$5 \times 10^{14}$	510	12	—	—	—
GaAs-89-47-2	$5 \times 10^{14}$	510	12	490	340	300
Wu & Wittry	$5 \times 10^{17}$	16	0.012		1.2	
Leitch <i>et al.</i>	$4 \times 10^{18}$	5.7	0.0015		3.1	
	$1 \times 10^{17}$	36	0.059		9.6	
	$2 \times 10^{17}$	25	0.029		3–14	

Since  $I_j$  was affected by extraneous phenomena at larger  $x$ , all slope calculations were based on  $\ln |I_j|$  versus  $x$  data at values of  $x$  found near the barrier (up to  $\leq 500 \mu\text{m}$ ). It is believed that this methodology was conservative and would actually tend to underestimate  $L_{p,n}$ . Values of  $L_{p,n}$  with related net carrier concentrations  $N$ , found from  $C$ - $V$  measurements, are shown in Table 1 for n-type GaAs and in Table 2 for p-type GaAs. Both tables include, for comparison, published values of  $L_{p,n}$ .

**5. Limiting Values of  $L_{p,n}$**

The upper limit of  $\tau_{p,n}$  can be set by the high probability of direct radiative recombination  $B_{\text{dr}}$  [equation (10) of Hall (1959)]:

$$B_{\text{dr}} = 0.58 \times 10^{-12} \bar{n} \left( \frac{m}{m_n + m_p} \right)^{\frac{3}{2}} \left( 1 + \frac{m}{m_n} + \frac{m}{m_p} \right) \left( \frac{300}{T} \right)^{\frac{3}{2}} W_G^2, \tag{4}$$

where  $\bar{n}$  is the refractive index,  $m_n, m_p$  are the density of states effective masses of electrons and holes, and  $W_G$  is the band gap. For GaAs at 300 K we have  $\bar{n} = 3.6$ ,  $m_n = 0.068$ ,  $m_p = 0.5$  and  $W_G = 1.45 \text{ eV}$ , so that  $B_{\text{dr}} = 1.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ .

Since the lifetime  $\tau_{\text{dr}} = 1/B_{\text{dr}} N$ , where  $n$  is the net carrier concentration, the lifetime increases as the net impurity level of the material decreases. Tables 1 and 2 include derived limiting values for  $L_{p,n}$  (and  $\tau_{p,n}$ ) as a means of comparing experimental results.

Of course when comparing experimental and theoretical values of  $L_{p,n}$  in Tables 1 and 2 it should be kept in mind that a large experimental error (about 50%) can be involved in this method of minority carrier diffusion length measurement. For example, surface recombination, thought to have had minimal effect on these results (see below), can increase the slope of the  $\ln |I_j|$  versus  $x$  plot near the barrier, thereby causing  $L_{p,n}$  to be underestimated. Likewise, the flatter  $L_2$  slopes noted far from the barrier (see above) can cause  $L_{p,n}$  to be overestimated—although this error was minimised here by measuring  $L_{p,n}$  closer to the barrier.

Sample geometry, which was not ideal, may also have affected the measured results if a situation intermediate to equations (1) and (2) had occurred, though in fact it was found that none of the data fitted a straight line in any segment using equation (2). An alternative to equation (2), given by Davidson and Dimitriadis (1980) and derived separately by Kuiken and Opdorp (1985), is

$$I_j \propto x^{-1/2} \exp(-x/L_{p,n}), \quad (5)$$

for the case of zero surface recombination velocity. For this equation our data do fit a straight line for large values of  $x$ , however, the resulting values of  $L_{p,n}$  are far in excess of the limiting values of  $L_{p,n}$ . The use of equation (1), which gives a better linear data fit than either equations (2) or (5), and which gives values of  $L_{p,n}$  in agreement with the limiting values, would therefore seem to be justified.

## 6. Discussion

Results obtained from EBIC measurements of LPE-GaAs show that the minority carrier lifetimes measured at 300 K are near the limiting theoretical values. To achieve this the material examined has to be of high purity, with low levels of non-radiative recombination centres. When comparing the material used for the Ryan and Eberhardt (1972)  $L_p$  measurements to material grown during this study, it appears to be of similar high purity. A further inquiry into the origin of their LPE-GaAs (Eberhardt *et al.* 1971; Hicks and Manley 1969) reveals that the epitaxial layer came from a Spectrosil silica crucible/Spectrosil furnace reaction tube growth system, similar to the arrangement used in our study. Further evidence for the high purity of the LPE material grown in our study comes from DLTS measurements of the epitaxial layers (Alexiev 1990). Those measurements examined the material over the temperature range from 380 to 11 K, and showed no deep level traps at a sensitivity of  $N_T \geq 10^{11} \text{ cm}^{-3}$ , confirming the high purity of the material. The use of the LPE material for X-ray and  $\gamma$ -ray detection also qualitatively indicates that the material is of high purity, with resolutions of 2–3 keV full width half maximum being achieved for 60 keV  $\gamma$ -rays at room temperature (Alexiev and Butcher 1992).

The flat response of  $\ln |I_j|$  versus  $x$  noted in sample GaAs-89-53-2 in Fig. 3 may have been the result of recombination at the site of a crystal defect or barrier breakdown due to the proximity of defects. Examination of the sample used showed surface abnormalities, including lineages near the barrier, which could contribute to this effect. At one point, approximately 50 to 100  $\mu\text{m}$  from the barrier, a sharp drop was noted in the measured value of  $I_j$  to about 10% of

the values shown in Fig. 3. Although the line of measurement to the barrier of sample GaAs-89-53-2 avoided this point, it was obvious that a large crystalline structure defect was present near the barrier. The high current otherwise shown by this sample may have been the result of diffusion of the minority carriers to the weak p-n junction formed between the epitaxy and the substrate (which was of course kept at a constant distance from the point source throughout the measurement).

The EBIC technique used for the measurement of the  $L_{p,n}$  values employed geometries which have not been well treated by theoretical studies. For our samples the electron beam was scanned perpendicular to the plane of the Schottky barrier (see Fig. 1), a situation treated by Ioannou and Dimitriadis (1982) and others for the specific case of zero depletion width. However, because of the large depletion widths of these samples, the carrier collection area was of the order of the electron beam penetration. A rigorous theoretical analysis of this situation is beyond the objective of this paper, however, the problem was addressed by comparing the measured data with the limiting cases provided by two existing models. The first limiting case is that of an electron beam scanned perpendicular to the plane of a Schottky barrier with zero depletion width; the second case is that of an electron beam scanned parallel to an infinite charge collection area—as occurs when scanning an electron beam parallel to a p-n junction. It was found that the second limiting model best fits our data, with the first model overestimating the values of  $L_{p,n}$ . To the accuracy expected here this treatment was adequate, though of course more rigorous models could improve the data analysis.

The effect of surface recombination was thought to have had minimal influence on the values of  $L_{p,n}$  found here. This is evidenced by the consistency of the measurements when different electron beam energies were used. For lower electron beam energies the point source of minority carriers generated in the semiconductor is closer to the surface. Therefore, if surface recombination had been a dominant feature of these devices, it would have caused a notable lowering of the measured values of  $L_{p,n}$  compared with the values found using a higher electron beam energy.

We note that the values of  $L_{p,n}$  measured are the highest so far reported for LPE-GaAs, indicating the high quality of the material produced.

## Conclusion

The diffusion length measurements reported here indicate that the LPE-GaAs samples being produced by the Australian Nuclear Science and Technology Organisation are of the highest quality for producing X-ray and low energy  $\gamma$ -ray radiation detectors. Values of the diffusion length measured for both p- and n-type GaAs were larger than any previously reported. These large diffusion lengths are a consequence of the low density of recombination centres present in the material; deep level transient spectrometry measurements of these samples confirm this assertion as the epitaxies are found to be free of any detectable deep level recombination centres.

The results reported here are in agreement with the theoretical values of diffusion length found using Hall's theory of recombination processes.



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