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# AUSTRALIAN NUCLEAR SCIENCE AND TECHNOLOGY ORGANISATION

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## ABSTRACT

Defects generated following Li diffusion into GaAs were studied by optical deep level transient spectroscopy (ODLTS) and deep level transient spectroscopy (DLTS). In an exploratory series of experiments, the effect of Li diffusion on existing trap spectra, defect generation and as a means for the compensation of GaAs was studied. The variables included diffusion temperature, initial trap spectra of GaAs and annealing periods. Detailed measurements of trap energies were made.

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DEFECTS; DIFFUSION; GALLIUM ARSENIDES; LITHIUM; SEMICONDUCTOR MATERIALS; SPECTROSCOPY

## EDITORIAL NOTE

The Australian Nuclear Science and Technology Organisation replaced the Australian Atomic Energy Commission on 27 April 1987. Reports issued after April 1987 have the prefix ANSTO with no change of the symbol (E, M, S or C) or numbering sequence.

## CONTENTS

## 1. INTRODUCTION

Lithium is an electrically active impurity in semiconductors which has been used to compensate p-type Ge and Si as, for example, in the manufacture of large volume single crystal co-axial Ge $\gamma$-detectors. Similarly, it is of scientific and technological interest to examine the behaviour of Li in the more complicated compound semiconductors. Fuller and Wolfstirn [1963] found that lithium behaves in GaAs as a self compensator. In contrast to the case of Ge or Si, where Li is a donor, Li in GaAs forms both donor and acceptor defects. These defects are controlled by initial concentrations of electrically active impurities and also the tendency of the Li to self compensate.

Fuller and Wolfstirn's model was determined experimentally by measuring the changes in the electron concentration when Li is out-diffused. They found that the introduction of two Li atoms caused a loss of one electron corresponding to a $(\text{Li}^+\text{Li}^-)$ pair. Acceptors remained after the Li was removed which, Fuller and Wolfstirn suggested, was due to Ga vacancies. Based on this earlier model, Norris and Narayanan [1977] suggested an alternative. They found, similarly, that when Li is out-diffused by annealing in air or in inert gas, all material became low resistivity p-type after the removal of the surface Li. They proposed that when Li enters into GaAs as an interstitial donor during the diffusion process, it forms substitutional acceptors $\text{Li}_i^+ + \text{V}_{\text{Ga}}^{=} + e^- \rightleftharpoons \text{Li}_{\text{Ga}}^{=}$. Pairing between $\text{Li}_i^+$ and $\text{Li}_{\text{Ga}}^{=}$ occurs when cooling to ambient temperature, with the formation of polyatomic acceptors and neutral complexes. Such a reaction can be best described by the following:

$$\text{Li}^+ + \text{Li}_{\text{Ga}}^{=} \rightleftharpoons (\text{Li}_i^+\,\text{Li}_{\text{Ga}}^{=})^- \quad ,$$

$$\text{Li}_i^+ + (\text{Li}_i^+\,\text{Li}_{\text{Ga}}^{=})^- \rightleftharpoons (2\text{Li}_i^+\,\text{Li}_{\text{Ga}}^{=})^\circ \quad ,$$

where i denotes an interstitial state, $^+$ and $^-$ indicate the charge state, and $^\circ$ indicates a neutral state.

When Li is out-diffused, the p-type behaviour of the material can be explained as follows. When the $\text{Li}_i^+$ donor is removed because of the dissociation of the complex, an acceptor is left behind. Levy and Spitzer [1973], on the other hand, found that after a comprehensive study of Li diffused defects five distinct complexes are formed: one donor, one acceptor and three neutral complexes. All complexes were shown to involve one or more Li atoms in association with two or more native vacancies. A possibility that other factors may play a part in donor-acceptor complex generation (for example, the introduction by diffusion of likely metallic contaminants, such as Na, K, Cu, Mg and Fe) was ruled out earlier by Fuller and Wolfstirn [1963] on two points. First, it is most improbable that such contaminants could be at a $10^{18}$ cm$^{-3}$ level, equal to the diffused Li concentration. Second, none of these elements, either in their elemental state or their oxide form, is known to produce acceptor states similar to Li. However, Si together with oxygen, a dominant impurity in zone and Czochralski grown material, may interact with Li since its behaviour is amphoteric in GaAs. When Si resides on a Ga site it will act as a donor and when on an As site it becomes an acceptor.

Such site transference has been implied in several studies, including the early work of Qulisser [1966] and Hwang [1968]. They reported that Si atoms may transfer from Ga to As sites *via* a vacancy by thermal induction; in one case, heavily doped GaAs was heated in hydrogen at 1050°C and in another lightly doped GaAs was heated in an evacuated quartz ampoule at 900°C. In both cases, it was assumed that the Si atoms transferred to the As site. Thus when Li approaches saturation, compensation may be achieved at the Ga site. However, Chen and Spitzer [1980] found experimentally that Li-native defect complexes are formed.

Results are presented of a series of diffusion experiments in which deep level Li generated defects in liquid-encapsulated Czochralski (LEC), GaAs and in n-type horizontal Bridgeman (HB) grown GaAs are examined by deep level transient spectroscopy (DLTS) techniques with the aim of compensating such material for radiation detector construction. Deep level transient capacitance (DLTC) and optical deep level transient spectroscopy (ODLTS) measurement techniques were used.

## 2. EXPERIMENTAL

### 2.1 Li Diffusion Effects in Semi-Insulating LEC GaAs

The liquid encapsulated LEC GaAs used in this study was purchased from Cambridge Instruments (UK). The material is semi-insulating and has a resistivity of greater than $10^6$ $\Omega$-cm. A net impurity density in the range of $10^{16}$ to $10^{17}$ $cm^{-3}$ is attributed to it by the manufacturer.

The material was prepared by standard methods. Briefly, a wafer is cut with a wire saw into 7 $mm^2$ sections. After lapping on 1200 grade SiC paper, the GaAs is polished on a lapping cloth with a 1500 grade metallurgical paste. After washing in an ultrasonic cleaner the GaAs is degreased in xylene, washed first in methanol and again in 18 MΩ water. The material is then etched in a warm (30 to 40°C) solution of $3H_2SO_4$:$1H_2O$:$1H_2O_2$ for four minutes. The resulting surface should be mirror-like with rounded corners. For device (Schottky diode) construction, metallisation of the GaAs section is accomplished by evaporating a 2 mm diameter gold rectifying contact on one surface and a full area aluminium ohmic contact over the opposite face. The inverse applies for p-type GaAs sections.

Semi-insulating LEC GaAs with a high resistivity was determined to be n-type by constructing a simple conduction counter with a 2 mm diameter gold window (front contact) and an aluminium full area (back contact) on the opposite face. When irradiated with an $^{241}$Am $\alpha$-particle, a spectrum was produced only when a negative polarity was applied to the front contact. This indicates that electrons are the dominant carriers and that holes are trapped. The $^{241}$Am $\alpha$-particle spectrum is shown for two types of conduction counter in **figure 1**. Both counters show poor 'diode' characteristics, differing by only a factor of 10 between the -ve versus +ve polarity because of high undepleted series resistance causing $V_D$ drop.

Three groups of chemically processed samples were prepared: one for Li diffusion-annealing, the second for annealing only and the third group as reference. Samples for Li diffusion-annealing were prepared by evaporating Li for 40 minutes onto both sides of the GaAs section while being heated at 400°C, and left to diffuse for 16 hours, followed by annealing at 400°C in 2%$H_2$-Ar gas for 96 hours. Samples for annealing only were similarly heated at 400°C in 2%$H_2$-Ar gas for 96 hours.

After each annealing cycle the GaAs samples were relapped and etched to remove the surface 'dissociation' layer. Afterwards, each sample was metallised and trap spectra were obtained using an optical deep level transient spectrometer [Alexiev and Tavendale 1984] which incorporates an exponential correlator [Miller *et al.* 1975, 1977] for signal processing. It is important to note that application of the Miller exponential correlator to ODLTS requires recalculation of the response function of the instrument. Details of the theoretical calculation for the modified response function are given in **appendix A**, which should be read in conjunction with Alexiev and Tavendale [1984].

## 2.2 Calculation of the Trap Energy Levels

The emission rate $e_{n,p}$ of a trapped carrier on a defect centre with an activation energy $E_T$ can be obtained from the detailed balanced relationship of a simple contracted exponential with a time constant $\tau_c$.

The balanced relationship can be expressed as

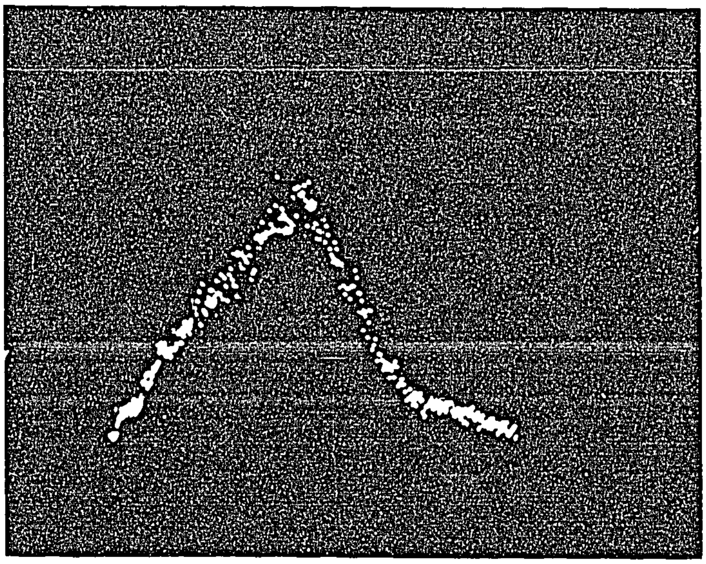
$$\frac{1}{\tau_c} = e_{n,p} = \frac{\sigma_{n,p} < v_{n,p} > N_c}{g} \exp - \left[ \frac{\Delta E}{kT} \right] .$$

$$\text{Thus} \quad \ell n \, \tau_c = \ell n \frac{g}{\sigma_{n,p} < v_{n,p} > N_c} + \frac{\Delta E}{kT}$$

$$= \text{constant} + \frac{\Delta E}{kT}$$

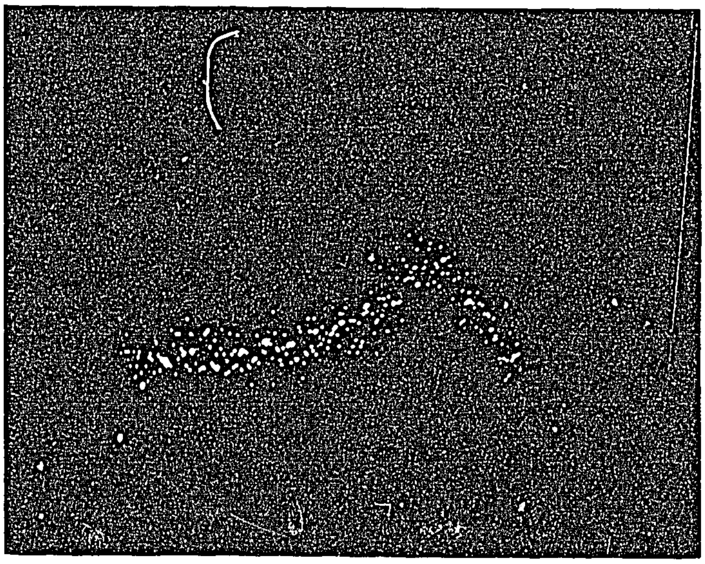
where $e_{n,p}$ is the emission rate of trap for electron/hole; $\sigma_{n,p}$ is the capture cross section of trap for electron/hole; $< v_{n,p} >$ is the average thermal velocity of electron/hole at temperature T; g is the degeneracy of trap; $N_c$ is the density of states in conduction band at T; $\Delta E$ is the energy separation of trap level from conduction band; and k is the Boltzmann's constant ($8.614 \times 10^{-5}$ eV $K^{-1}$).

(a)



Au 2 mm $\phi$ front // Al back contact, EHT=-500 volts.
No $\alpha$-particle counts observed when +ve volts applied.

(b)



Al 2 mm $\phi$ front // Au back contact, EHT=-250 volts.
No $\alpha$-particle counts observed when +ve volts applied.

Figure 1 Americium-241 $\alpha$-particle spectrum produced by a simple conduction counter used to determine polarity of the LEC GaAs.

A plot of $\ell n\, \tau_c$ v. 1/T will have a slope of $\Delta E/k$. Thus, trap energy $\Delta E$ (eV) = slope x k. This is corrected for the $T^2$ dependence of $< v_n > N_c$ by subtracting $2kT_{av}$, where $T_{av}$ is the average temperature over which the data are collected.

### 2.3 Estimation of Trap Energies ($E_T$) for Li Diffused Semi-Insulating LEC GaAs

An estimate of emission rate for the hole trap spectra (**figure 2a**) was obtained:

$H_1$ = 0.31 eV
$H_2$ = 0.43 eV
$H_3$ = 0.26 eV
$H_4$ = resolution was inadequate for measurement.

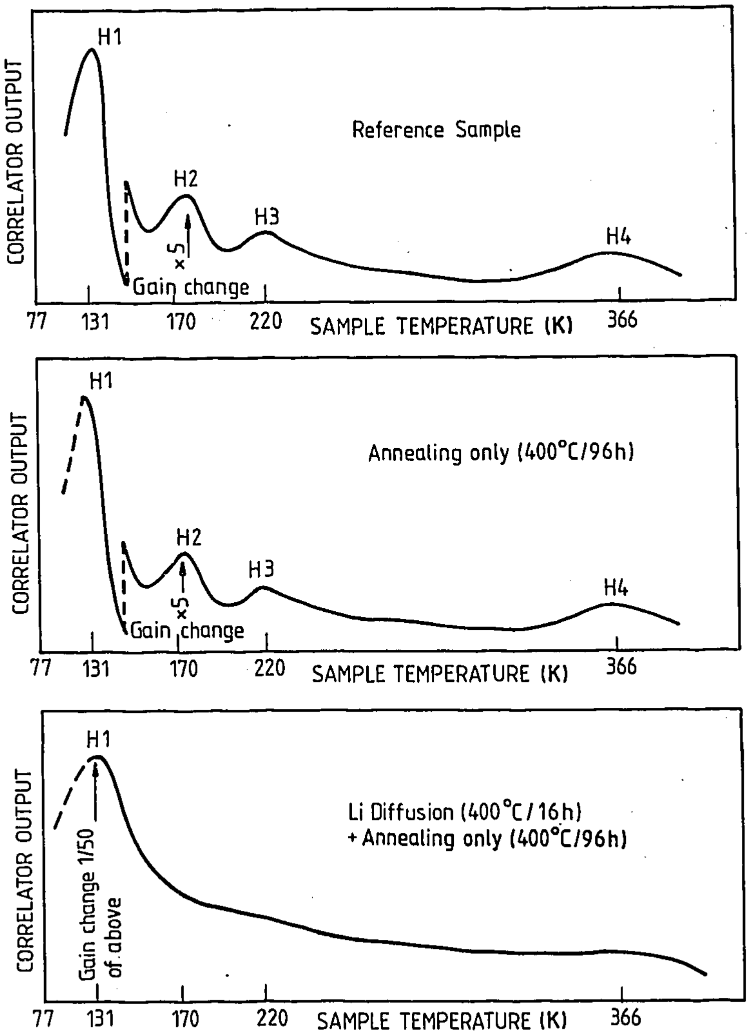


Figure 2a ODLTS hole trap spectra of n-type semi-insulating GaAs.

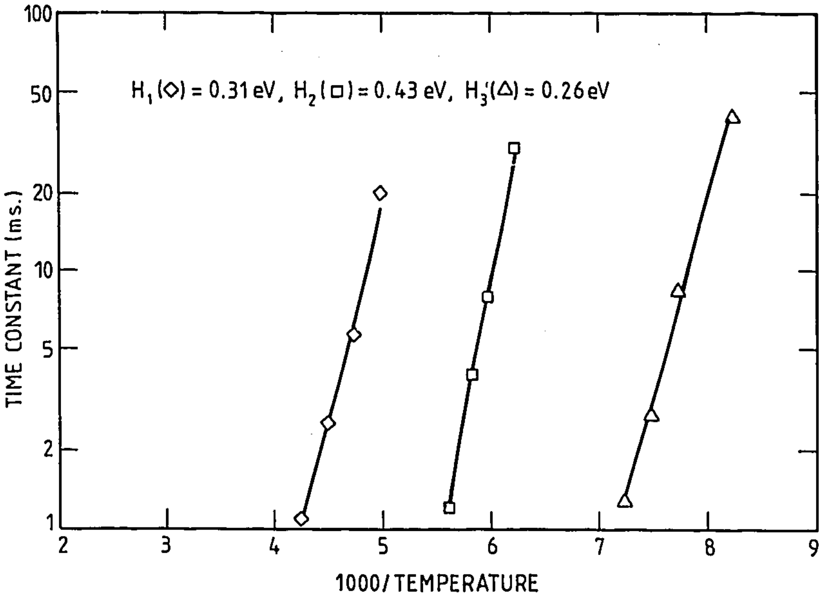


Figure 2b Arrhenius plot of n-type semi-insulating GaAs.

The emission rate data are shown in **figure 2b** as $H_1$, $H_2$ and $H_3$ in the plane of $\ln \tau_{Sm}$ plotted against 1000/T (K), where $\ln \tau_{Sm}$ is the corrected time constant as derived in **appendix A**; the straight lines are the results of least-mean-square fitting of experimental points. For comparison, previously reported analyses of hole trap emission rates found by other laboratories were given by Mitonneau *et al.* [1977], a version of which is reproduced in **figure 2c.**

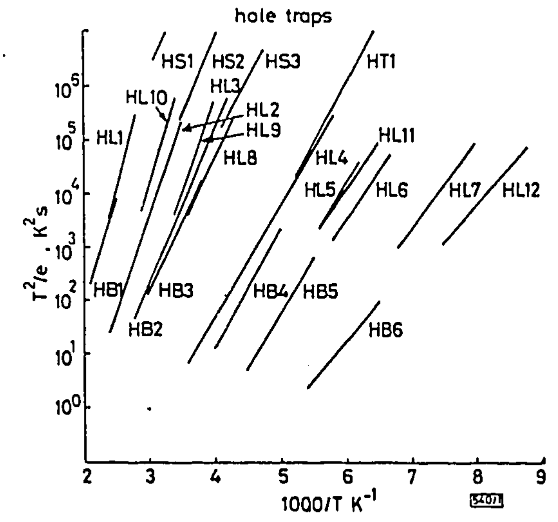


Figure 2c Plots of $T^2/e_p$ as function of 1/T for all hole traps

T: University of Tokyo, S: University of Sheffield, B: Bell Telephone Laboratories, L: this work. The curves B giving Lang's results are extrapolated from his DLTS spectra [after Mitonneau et al. 1977].

## 2.4 Comparison of Hole Emission Rates from Traps

Variations of reported data by Mitonneau *et al.* must be assumed since line position may vary because of experimental errors, calibration error and other factors; thus a broad error of about 20 per cent is used in the hole trap energy comparison shown in **table 1**.

TABLE 1

HOLE TRAP ENERGY

| Hole Trap | Activation Energy (eV) | Compared Trap | Type of Sample | Energy (eV) | Impurity Defect |
|---|---|---|---|---|---|
| $H_1$ | 0.31 | HL7 | As-grown m.b.e. | 0.35 | native |
| | | LH11 | Melt growth | 0.35 | native |
| $H_2$ | 0.43 | HL4 | Cu-diffused v.p.e. | 0.42 | Cu imp. |
| | | LH5 | As-grown l.p.e. | 0.41 | native |
| $H_3$ | 0.26 | HL12 | Zn-contaminated v.p.e. | 0.27 | Zn imp. |

v.p.e. - vapour phase epitaxy
l.p.e. - liquid phase expitaxy
m.b.e. - molecular beam epitaxy
imp. - impurity

Trap densities and cross sections could not be measured with the ODLTS. However, a measure of relative density can be gauged from the amplitude of spectral peaks taken at known gain conditions. It is clear that the material is dominated by hole trap $H_1$ which can be taken as a native defect, and is most likely responsible for the high resistivity of this material. Traps $H_2$ and $H_3$ correspond to impurity defects of Cu and Zn. By comparison with $H_1$, the concentration of these traps is much lower (20:1) so they cannot be thought of as significant recombination centres.

Influence of the diffused Li became apparent in the spectral response only after the GaAs was annealed for 96 h. Again hole trap $H_1$ played a dominant role and increased considerably in magnitude. When a companion sample of GaAs (no Li) was annealed, no alteration was noted in the trap magnitude.

It is possible that a similar mechanism, as noted previously by Chen and Spitzer [1980], is active; namely, that the Li affects the shallow donor Si site transference and is substitutional on a created vacancy which in turn may be represented by the native defect $H_1$. The fact that no new Li defects were noted is contrary to Chen and Spitzer; however, if they had been created, these levels may well have been swamped by the dominant trap level $H_1$, as illustrated in **figure 1**. Two other batches of LEC (undoped) semi-insulating GaAs were similarly treated and produced with almost identical results.

## 2.5 Li Diffusion Effects in Horizontal Bridgman Grown GaAs

A section of commercially produced bulk GaAs ($N_D \sim 10^{16}$ cm$^{-3}$) from Cambridge Instruments (UK), was selected for Li diffusion. Since the material was not semi-insulating, conventional DLTS, capacitance-voltage (C-V) and therefore net carrier concentration (N(x)) measurements could be applied.

Although the GaAs was polycrystalline, it contained large volumes of single crystals which were easily selected and diodes processed in the conventional manner previously described. These diodes proved to have good current-voltage (I-V) and capacitance-voltage (C-V) characteristics as shown in **figure 3**. A DLTS spectrum was obtained (**figure 4**). The deep levels are typical of an electron trap spectrum found in n-type GaAs grown by vapour-phase epitaxy and in bulk material. Three deep donors have been identified and are shown in **table 2** and a related model for compensation is shown in **figure 5**.

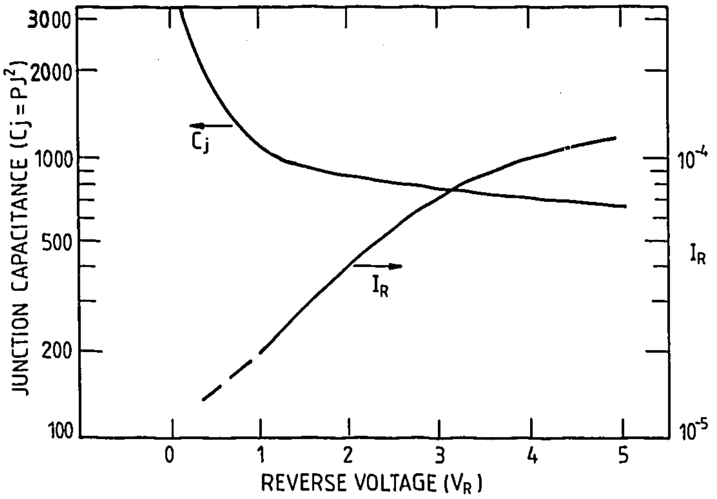


Figure 3 $I_R - V_R$ and $C_j - V_R$ for n-type Schottky GaAs diode

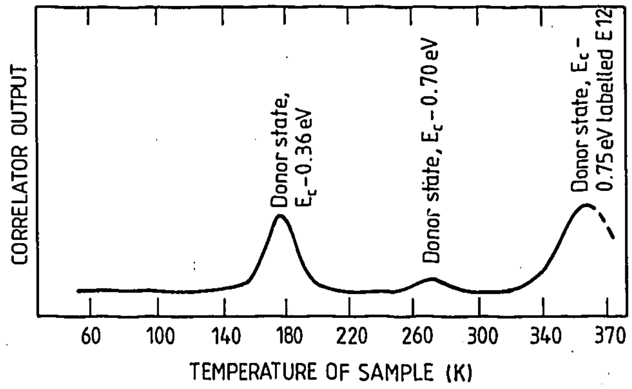


Figure 4 Electron trap spectrum for (HB) n-type GaAs

## TABLE 2
## DEEP DONORS IN (HB) n-TYPE GaAs

| Type | Level (eV) | Trap Density ($N_T$ cm$^{-3}$) | Association | References |
|---|---|---|---|---|
| Deep donor | 0.36 | $2.8 \times 10^{14}$ | bulk native defect | Martin *et al.* [1977] |
| Deep donor | 0.70 | $2.1 \times 10^{15}$ | $O_2$ related | Martin *et al.* [1977] |
| Deep donor | 0.75 | - | EL2 | Martin *et al.* [1977] |
| Not observed but always associated in n-type GaAs ($10^8$ Ω-cm) | | | | |
| Shallow donor | 0.006 | - | Si | Weiner *et al.* [1972] |
| Shallow acceptor | 0.019 | - | $C^{12}$ | Oliver *et al.* [1981] |

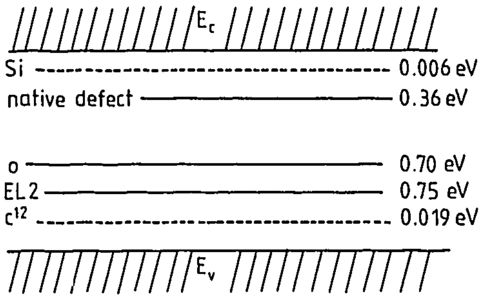


Figure 5 Model for compensation in (HB) n-type GaAs

Such centres are frequently encountered in n-type GaAs and have received much attention in recent studies of the compensating mechanisms in semi-insulating material. The EL2 trap, called the main electron trap, has been found in epitaxial, bulk and vapour phase material and in high-resistivity material. It is responsible for compensating the shallow Si acceptor and clamping the Fermi level in Schottky barriers [Spicer *et al.* 1980]. Also of ongoing interest is the possibility that the residual impurity, oxygen, is associated with the EL2 defect. It is known that Si, and for that matter also B, is a contamination primarily derived from the interaction of the melt with the encapsulant $B_2O_3$ and the crucible $SiO_2$. The presence of [OH] in the encapsulant may suppress the reduction of $SiO_2$ and $B_2O_3$, thus inhibiting the Si and B contamination. In the HB technique oxygen can be derived from a small quantity of $Ga_2O_3$, similarly inhibiting Si centres.

Speculation that oxygen plays an important role in producing semi-insulating properties was developed on this basis. However, data published by Huber [1979] indicate the contrary and exclude oxygen as a centre responsible for EL2. The work by Pursey *et al.* [1981] on trap-free melt-grown GaAs also excludes the influence of oxygen. It suggests that the remedy lies in low-dislocation growth of the material by precise control of optimum arsenic vapour pressure, as well as the reduction of free vacancies by adding $1Ga_2O_3 : 10^5$ GaAs, thereby suggesting that an oxygen-vacancy interaction occurs.

The influence of thermal annealing on EL2 has been noted in this work; when the n-type GaAs (HB grown) was annealed at 850°C/20 h, the material became compensated and exhibited high resistivity. An ODLTS spectrum showed (**figure 6**) that new electron trap levels were produced with no alteration to the EL2 centre. It is clear that annealing altered the stoichiometry of the crystal simply by a GaAs redistribution within its solid phase.

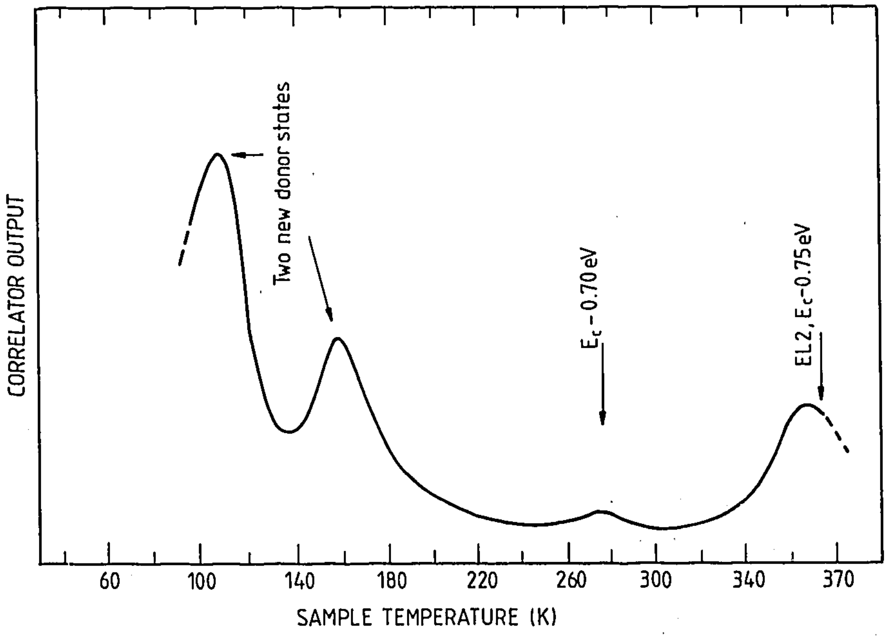


Figure 6 ODLTS electron trap spectrum of annealed (HB) n-type GaAs ($\tau_{COR}$ = 10 m s)

Similarly, n-type GaAs (HB grown) material was subjected to Li diffusion, as described earlier. The GaAs(Li) was again annealed at 850°C/20 h. The resulting samples were processed and an ODLTS spectrum taken: the GaAs(Li) did not produce additional levels to the n-type GaAs (HB grown) annealed only samples. GaAs(Li) also remained semi-insulating.

The net carrier concentration (C-V) was measured and calculated. The depletion depth, limited by the maximum $V_R$ applicable to the diode, could be measured only to a depth of 1.5 μm resulting in no significant alteration (compensation) when Li was diffused at 400°C.

Average N(x) values obtained for n-type (HB) GaAs

$$N(x) \approx 2 \times 10^{16}\,\mathrm{cm}^{-3}\ .$$

Average N(x) values obtained for n-type (HB) Li diffused GaAs

$$N(x) \approx 3 \times 10^{16}\,\mathrm{cm}^{-3}\ .$$

## 3. CONCLUSIONS

One of the prime purposes for studying Li diffusion in GaAs was to investigate the effect of Li on localised defect states and to use it as a means of compensating the residual electrical active impurities in (LEC) semi-insulating GaAs and (HB) n-type GaAs.

It was found that after annealing the as-grown untreated (HB) n-type GaAs for 20 h, the sample became semi-insulating. Two additional electron trap levels were formed with no change to the intrinsic electron trap spectrum: here, attention was centred on interaction with Li with trap EL2 commonly found in such material. When Li was diffused no change was noted to the electron trap spectra; the material remained semi-insulating.

When Li was diffused in the (LEC) semi-insulating GaAs and then subsequently annealed, a significant increase in magnitude was produced to the hole trap $H_1$, thought to be a native defect. No significant compensation was noted to the residual impurity level with Li diffusion-annealing in both types of GaAs.

## 4. ACKNOWLEDGEMENTS

The authors wish to thank Mr A.A. Williams for DLTS and computational support.

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## APPENDIX A

## CALCULATION OF THE RESPONSE OF A MILLER EXPONENTIAL SIGNAL CORRELATOR TO ODLT SIGNALS

The Miller exponential signal correlator used for the deep level transient spectroscopy measurements described in this report was originally designed to process simple time varying signals of the type exp(-t/$\tau_S$), where $\tau_S$ is a trap emission period, such as are generated in a DLT capacitance spectrometer system. However, when applied to inspect signals from an ODLT system such as we used here for semi-insulating GaAs [marginal oscillator - ODLT system, Alexiev and Tavendale 1984], it is necessary to recalculate the Miller correlator response function. In this application, the time varying signal generated by the photo-induced trap-emission modulated sample conductance, which is the parameter of interest for the device under test, varies as the product of 1/$\tau_S$ exp(–t/$\tau_S$).

The theoretical derivation of the modified response function given here employs the symbolism used by Miller *et al.* [1975]; it should be noted that there is an error in **equation 3.1** of that reference - the final term of the equation should read

$$\frac{T_R\,T_S}{T_M\,(T_R + T_S)}$$

in their treatment of the response of the correlator to standard exponentially decaying signals.

The general form of the photoconductance transient signal (*i.e.* as generated by a pulse of light) is given by:

$$I(t) = \frac{A\,e^{-t/\tau_s}}{\tau_s} \quad ,$$

where A is the constant, $\tau_S$ is the decay time, and I(t) is the intensity of light pulse.

The exponential correlator response is then

$$R = \int_{\tau_H}^{\tau_m} \frac{A\,e^{-t/\tau_s}}{\tau_s} \cdot e^{-t/\tau_R}\,dt \quad ,$$

where $\tau_H$ is the holding time, $\tau_R$ is the correlator time constant, and $\tau_m$ is the restoration time constant (which is set experimentally to $\tau_m$ = 2.06 $\tau_R$), thus, with base-line restoration, gives an amplitude factor,

$$\frac{A\,e^{-t/\tau_S}}{\tau_S} - \frac{A\,e^{-\tau_m/\tau_S}}{\tau_S} \quad .$$

Thus,

$$R = \frac{A}{\tau_S} \int_{\tau_H}^{\tau_m} \left[ e^{-t/\tau_s} - e^{-\tau_m/\tau_s} \right] e^{-t/\tau_R}\,dt \quad .$$

Let A = 1 and $I_1$, $I_2$ be terms in the integrant

$$\begin{aligned} I_1 &= \int_{\tau_H}^{\tau_m} e^{-t/\tau_S} \cdot e^{-t/\tau_R}\,dt \\ &= \int_{\tau_H}^{\tau_m} e^{-t/\tau_1}\,dt \qquad \text{where } \frac{1}{\tau_1} = \frac{1}{\tau_S} + \frac{1}{\tau_e} \\ &= \left[ -\tau_1\,e^{-t/\tau_1} \right]_{\tau_H}^{\tau_m} \\ &= \tau_1 \left( e^{-\tau_H/\tau_1} - e^{-\tau_m/\tau_1} \right) \quad . \end{aligned}$$

Similarly

$$\begin{aligned} I_2 &= -\int_{\tau_H}^{\tau_m} e^{-\tau_m/\tau_S} \cdot e^{-t/\tau_R}\,dt \\ &= -\Big[-\tau_R\, e^{-\tau_m/\tau_S} \cdot e^{-t/\tau_R}\Big]_{\tau_H}^{\tau_m} \\ &= \tau_R\Big( e^{-\tau_m/\tau_1} - e^{-(\tau_H/\tau_R+\tau_m/\tau_S)}\Big) \quad . \end{aligned}$$

Thus

$$\begin{aligned} R &= \frac{I_1 + I_2}{\tau_S} \\ &= \frac{\tau_1}{\tau_S}\Big( e^{-\tau_H/\tau_1} - e^{-\tau_m/\tau_1}\Big) + \frac{\tau_R}{\tau_S}\Big( e^{-\frac{\tau_m}{\tau_1}} - e^{-(\frac{\tau_H}{\tau_R}+\frac{\tau_m}{\tau_S})}\Big) \quad . \end{aligned}$$

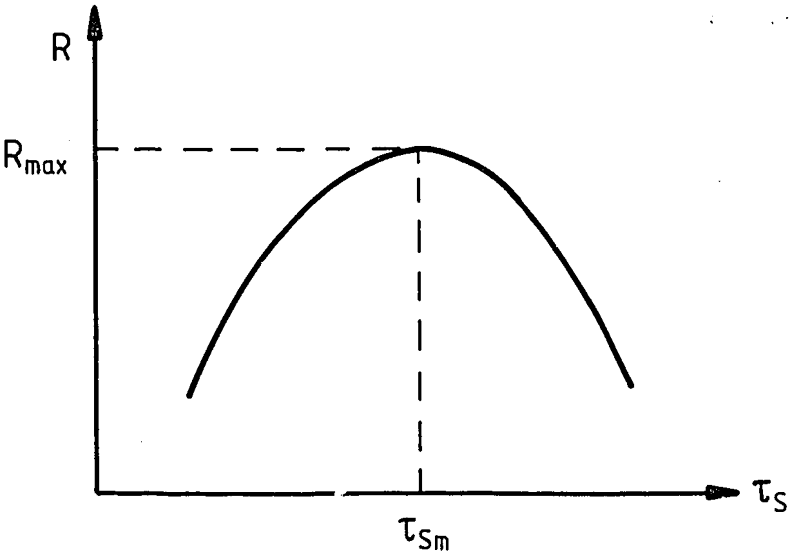
Substituting

$$\frac{1}{\tau_1} = \frac{1}{\tau_S} + \frac{1}{\tau_R}$$

the expression can be rewritten to

$$\begin{aligned} R = e^{-\frac{\tau_m(\tau_R+\tau_S)}{\tau_R\tau_S}} \cdot \left\{ -\left(\frac{\tau_R}{\tau_R+\tau_S}\right) + \frac{\tau_R}{\tau_S}\right\} + e^{-\frac{\tau_H(\tau_R+\tau_S)}{\tau_R\tau_S}} \\ \cdot \left\{\frac{\tau_R}{\tau_R+\tau_S}\right\} - e^{-\frac{(\tau_H\tau_S+\tau_R\tau_m)}{\tau_R\tau_S}} \cdot \left\{\frac{\tau_R}{\tau_S}\right\} \quad . \end{aligned}$$

Thus, solving for R in terms of $\tau_R$ and $\tau_S$ fixed to a value, with $\tau_H$ = holding time also fixed to a value and $\tau_m = 2.06\,\tau_R$ then R will maximise as shown diagrammatically:



Then, by plotting the value $\tau_{Sm}$ *v.* $\tau_S$ a correction curve for the exponential correlation can be obtained.

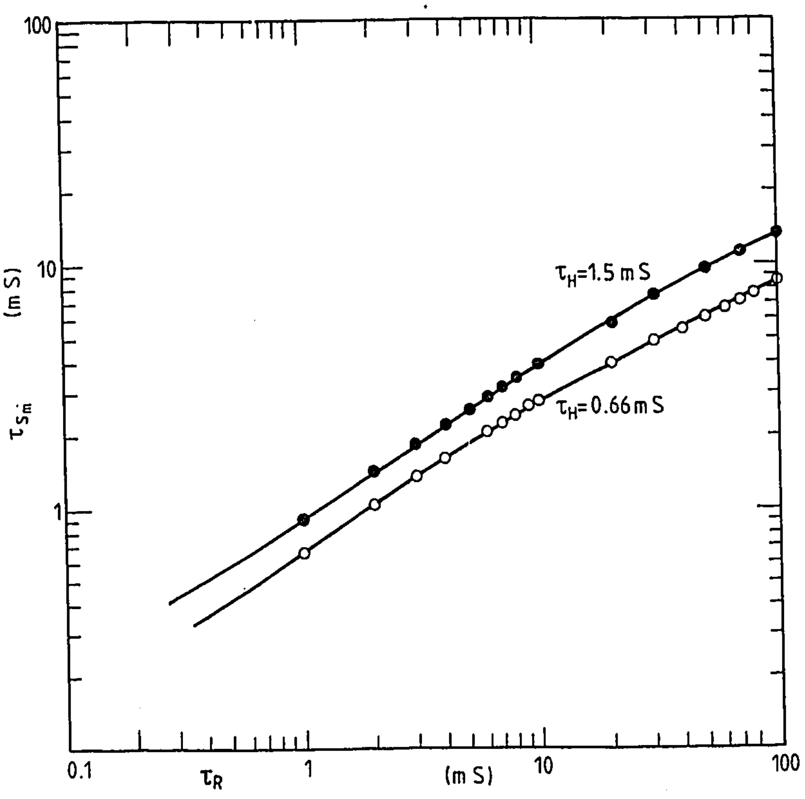


Figure A1 Correction curve for the exponential correlator for the parameters used in this report (where $\tau_H = 0.66$ ms and $\tau_m = 2.06\,\tau_R$).

The value of $\tau_{Sm}$ (for a particular value of $\tau_R$) can now be used for trap energy calculations in the relationship $\ell n\, \tau_{Sm} = \text{constant} + \frac{\Delta E}{kT}$.

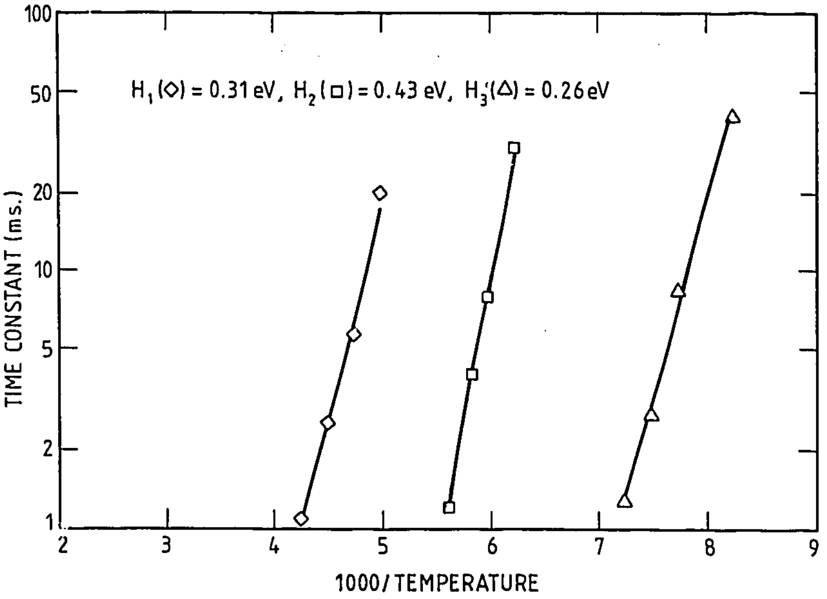


Figure 2b Arrhenius plot of n-type semi-insulating GaAs.

The emission rate data are shown in **figure 2b** as $H_1$, $H_2$ and $H_3$ in the plane of $\ell n\, \tau_{Sm}$ plotted against 1000/T (K), where $\ell n\, \tau_{Sm}$ is the corrected time constant as derived in **appendix A**; the straight lines are the results of least-mean-square fitting of experimental points. For comparison, previously reported analyses of hole trap emission rates found by other laboratories were given by Mitonneau *et al.* [1977], a version of which is reproduced in **figure 2c**.

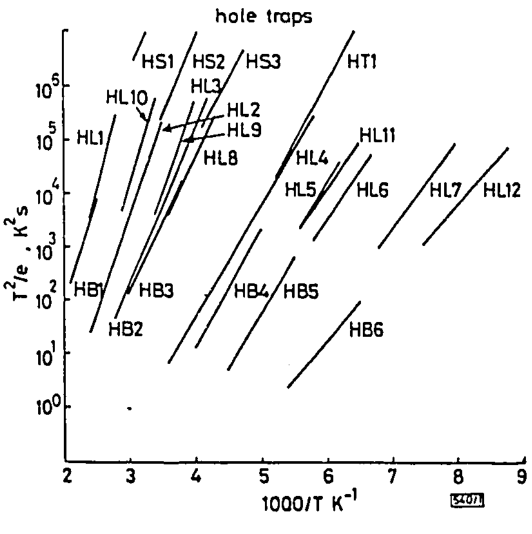


Figure 2c Plots of $T^2/e_p$ as function of 1/T for all hole traps

T: University of Tokyo, S: University of Sheffield, B: Bell Telephone Laboratories, L: this work. The curves B giving Lang's results are extrapolated from his DLTS spectra [after Mitonneau et al. 1977].

## 2.4 Comparison of Hole Emission Rates from Traps

Variations of reported data by Mitonneau *et al.* must be assumed since line position may vary because of experimental errors, calibration error and other factors; thus a broad error of about 20 per cent is used in the hole trap energy comparison shown in **table 1**.

**TABLE 1**

**HOLE TRAP ENERGY**

| Hole Trap | Activation Energy (eV) | Compared Trap | Type of Sample | Energy (eV) | Impurity Defect |
|---|---|---|---|---|---|
| $H_1$ | 0.31 | HL7 | As-grown m.b.e. | 0.35 | native |
| | | LH11 | Melt growth | 0.35 | native |
| $H_2$ | 0.43 | HL4 | Cu-diffused v.p.e. | 0.42 | Cu imp. |
| | | LH5 | As-grown l.p.e. | 0.41 | native |
| $H_3$ | 0.26 | HL12 | Zn-contaminated v.p.e. | 0.27 | Zn imp. |

v.p.e. - vapour phase epitaxy
l.p.e. - liquid phase expitaxy
m.b.e. - molecular beam epitaxy
imp. - impurity

Trap densities and cross sections could not be measured with the ODLTS. However, a measure of relative density can be gauged from the amplitude of spectral peaks taken at known gain conditions. It is clear that the material is dominated by hole trap $H_1$ which can be taken as a native defect, and is most likely responsible for the high resistivity of this material. Traps $H_2$ and $H_3$ correspond to impurity defects of Cu and Zn. By comparison with $H_1$, the concentration of these traps is much lower (20:1) so they cannot be thought of as significant recombination centres.

Influence of the diffused Li became apparent in the spectral response only after the GaAs was annealed for 96 h. Again hole trap $H_1$ played a dominant role and increased considerably in magnitude. When a companion sample of GaAs (no Li) was annealed, no alteration was noted in the trap magnitude.

It is possible that a similar mechanism, as noted previously by Chen and Spitzer [1980], is active; namely, that the Li affects the shallow donor Si site transference and is substitutional on a created vacancy which in turn may be represented by the native defect $H_1$. The fact that no new Li defects were noted is contrary to Chen and Spitzer; however, if they had been created, these levels may well have been swamped by the dominant trap level $H_1$, as illustrated in **figure 1**. Two other batches of LEC (undoped) semi-insulating GaAs were similarly treated and produced with almost identical results.

## 2.5 Li Diffusion Effects in Horizontal Bridgman Grown GaAs

A section of commercially produced bulk GaAs ($N_D \sim 10^{16}$ cm$^{-3}$) from Cambridge Instruments (UK), was selected for Li diffusion. Since the material was not semi-insulating, conventional DLTS, capacitance-voltage (C-V) and therefore net carrier concentration (N(x)) measurements could be applied.

Although the GaAs was polycrystalline, it contained large volumes of single crystals which were easily selected and diodes processed in the conventional manner previously described. These diodes proved to have good current-voltage (I-V) and capacitance-voltage (C-V) characteristics as shown in **figure 3**. A DLTS spectrum was obtained (**figure 4**). The deep levels are typical of an electron trap spectrum found in n-type GaAs grown by vapour-phase epitaxy and in bulk material. Three deep donors have been identified and are shown in **table 2** and a related model for compensation is shown in **figure 5**.

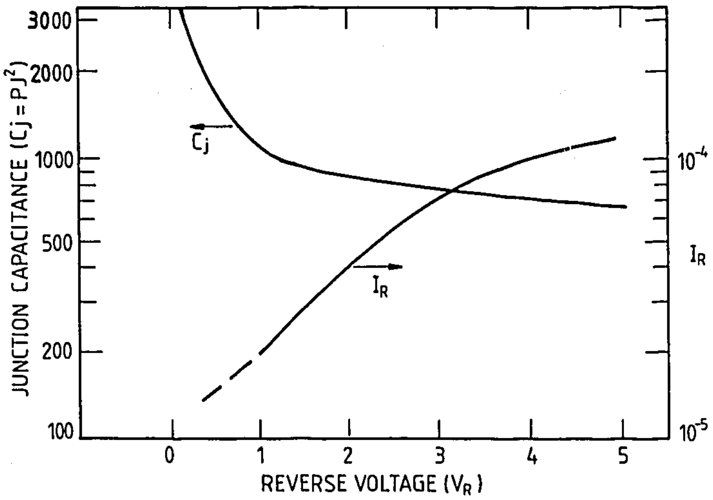


Figure 3 $I_R - V_R$ and $C_j - V_R$ for n-type Schottky GaAs diode

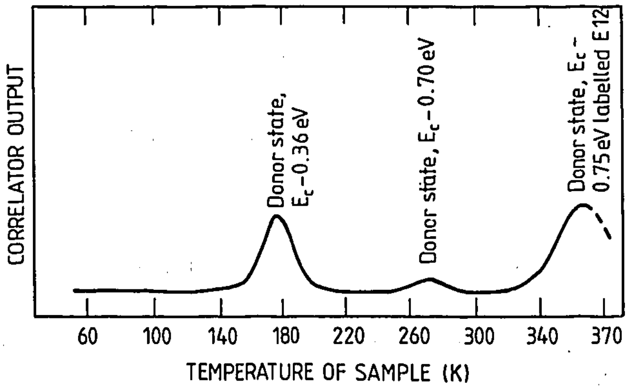


Figure 4 Electron trap spectrum for (HB) n-type GaAs

## TABLE 2

## DEEP DONORS IN (HB) n-TYPE GaAs

| Type | Level (eV) | Trap Density ($N_T$ cm$^{-3}$) | Association | References |
|---|---|---|---|---|
| Deep donor | 0.36 | $2.8 \times 10^{14}$ | bulk native defect | Martin *et al.* [1977] |
| Deep donor | 0.70 | $2.1 \times 10^{15}$ | $O_2$ related | Martin *et al.* [1977] |
| Deep donor | 0.75 | - | EL2 | Martin *et al.* [1977] |
| Not observed but always associated in n-type GaAs ($10^8$ Ω-cm) | | | | |
| Shallow donor | 0.006 | - | Si | Weiner *et al.* [1972] |
| Shallow acceptor | 0.019 | - | $C^{12}$ | Oliver *et al.* [1981] |

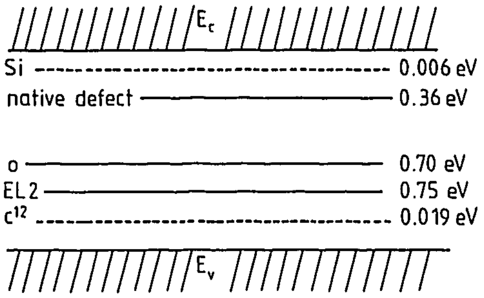


Figure 5 Model for compensation in (HB) n-type GaAs

Such centres are frequently encountered in n-type GaAs and have received much attention in recent studies of the compensating mechanisms in semi-insulating material. The EL2 trap, called the main electron trap, has been found in epitaxial, bulk and vapour phase material and in high-resistivity material. It is responsible for compensating the shallow Si acceptor and clamping the Fermi level in Schottky barriers [Spicer *et al.* 1980]. Also of ongoing interest is the possibility that the residual impurity, oxygen, is associated with the EL2 defect. It is known that Si, and for that matter also B, is a contamination primarily derived from the interaction of the melt with the encapsulant $B_2O_3$ and the crucible $SiO_2$. The presence of [OH] in the encapsulant may suppress the reduction of $SiO_2$ and $B_2O_3$, thus inhibiting the Si and B contamination. In the HB technique oxygen can be derived from a small quantity of $Ga_2O_3$, similarly inhibiting Si centres.

Speculation that oxygen plays an important role in producing semi-insulating properties was developed on this basis. However, data published by Huber [1979] indicate the contrary and exclude oxygen as a centre responsible for EL2. The work by Pursey *et al.* [1981] on trap-free melt-grown GaAs also excludes the influence of oxygen. It suggests that the remedy lies in low-dislocation growth of the material by precise control of optimum arsenic vapour pressure, as well as the reduction of free vacancies by adding $1Ga_2O_3 : 10^5$ GaAs, thereby suggesting that an oxygen-vacancy interaction occurs.

The influence of thermal annealing on EL2 has been noted in this work; when the n-type GaAs (HB grown) was annealed at 850°C/20 h, the material became compensated and exhibited high resistivity. An ODLTS spectrum showed (**figure 6**) that new electron trap levels were produced with no alteration to the EL2 centre. It is clear that annealing altered the stoichiometry of the crystal simply by a GaAs redistribution within its solid phase.

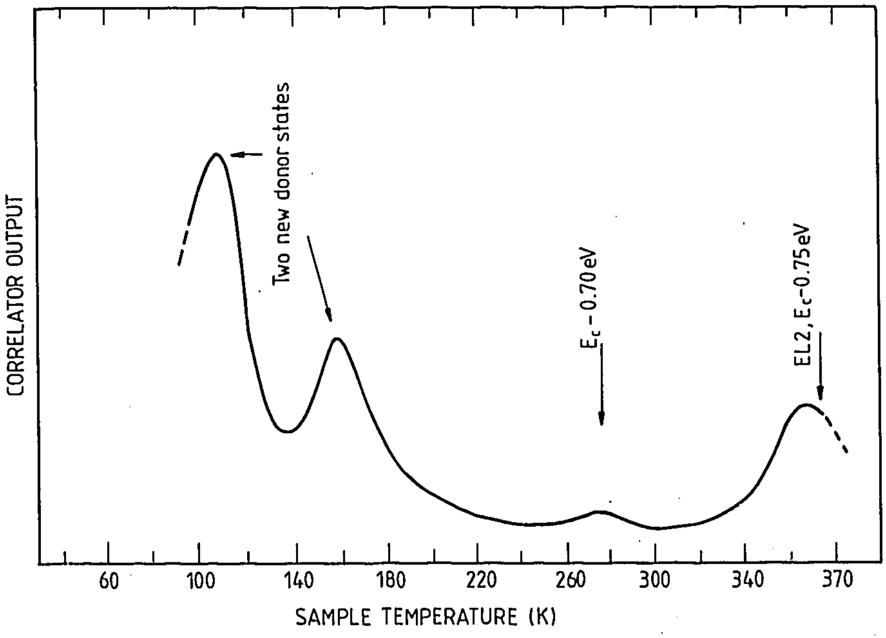


Figure 6 ODLTS electron trap spectrum of annealed (HB) n-type GaAs ($\tau_{COR}$ = 10 m s)

Similarly, n-type GaAs (HB grown) material was subjected to Li diffusion, as described earlier. The GaAs(Li) was again annealed at 850°C/20 h. The resulting samples were processed and an ODLTS spectrum taken: the GaAs(Li) did not produce additional levels to the n-type GaAs (HB grown) annealed only samples. GaAs(Li) also remained semi-insulating.

The net carrier concentration (C-V) was measured and calculated. The depletion depth, limited by the maximum $V_R$ applicable to the diode, could be measured only to a depth of 1.5 μm resulting in no significant alteration (compensation) when Li was diffused at 400°C.

Average N(x) values obtained for n-type (HB) GaAs

$$N(x) \approx 2 \times 10^{16}\,\mathrm{cm}^{-3} .$$

Average N(x) values obtained for n-type (HB) Li diffused GaAs

$$N(x) \approx 3 \times 10^{16}\,\mathrm{cm}^{-3} .$$

## 3. CONCLUSIONS

One of the prime purposes for studying Li diffusion in GaAs was to investigate the effect of Li on localised defect states and to use it as a means of compensating the residual electrical active impurities in (LEC) semi-insulating GaAs and (HB) n-type GaAs.

It was found that after annealing the as-grown untreated (HB) n-type GaAs for 20 h, the sample became semi-insulating. Two additional electron trap levels were formed with no change to the intrinsic electron trap spectrum: here, attention was centred on interaction with Li with trap EL2 commonly found in such material. When Li was diffused no change was noted to the electron trap spectra; the material remained semi-insulating.

When Li was diffused in the (LEC) semi-insulating GaAs and then subsequently annealed, a significant increase in magnitude was produced to the hole trap $H_1$, thought to be a native defect. No significant compensation was noted to the residual impurity level with Li diffusion-annealing in both types of GaAs.

## 4. ACKNOWLEDGEMENTS

The authors wish to thank Mr A.A. Williams for DLTS and computational support.

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# APPENDIX A

## CALCULATION OF THE RESPONSE OF A MILLER EXPONENTIAL SIGNAL CORRELATOR TO ODLT SIGNALS

The Miller exponential signal correlator used for the deep level transient spectroscopy measurements described in this report was originally designed to process simple time varying signals of the type exp($-t/\tau_S$), where $\tau_S$ is a trap emission period, such as are generated in a DLT capacitance spectrometer system. However, when applied to inspect signals from an ODLT system such as we used here for semi-insulating GaAs [marginal oscillator - ODLT system, Alexiev and Tavendale 1984], it is necessary to recalculate the Miller correlator response function. In this application, the time varying signal generated by the photo-induced trap-emission modulated sample conductance, which is the parameter of interest for the device under test, varies as the product of $1/\tau_S$ exp($-t/\tau_S$).

The theoretical derivation of the modified response function given here employs the symbolism used by Miller *et al.* [1975]; it should be noted that there is an error in **equation 3.1** of that reference - the final term of the equation should read

$$\frac{T_R\,T_S}{T_M\,(T_R + T_S)}$$

in their treatment of the response of the correlator to standard exponentially decaying signals.

The general form of the photoconductance transient signal (*i.e.* as generated by a pulse of light) is given by:

$$I(t) = \frac{A\,e^{-t/\tau_s}}{\tau_s} \quad ,$$

where A is the constant, $\tau_S$ is the decay time, and I(t) is the intensity of light pulse.

The exponential correlator response is then

$$R = \int_{\tau_H}^{\tau_m} \frac{A\,e^{-t/\tau_s}}{\tau_s} \cdot e^{-t/\tau_R}\,dt \quad ,$$

where $\tau_H$ is the holding time, $\tau_R$ is the correlator time constant, and $\tau_m$ is the restoration time constant (which is set experimentally to $\tau_m = 2.06\ \tau_R$), thus, with base-line restoration, gives an amplitude factor,

$$\frac{A\,e^{-t/\tau_S}}{\tau_S} - \frac{A\,e^{-\tau_m/\tau_S}}{\tau_S} \quad .$$

Thus,

$$R = \frac{A}{\tau_S} \int_{\tau_H}^{\tau_m} \left[ e^{-t/\tau_S} - e^{-\tau_m/\tau_S} \right] e^{-t/\tau_R}\,dt \quad .$$

Let $A = 1$ and $I_1$, $I_2$ be terms in the integrant

$$\begin{aligned} I_1 &= \int_{\tau_H}^{\tau_m} e^{-t/\tau_S} \cdot e^{-t/\tau_R}\,dt \\ &= \int_{\tau_H}^{\tau_m} e^{-t/\tau_1}\,dt \qquad \text{where } \frac{1}{\tau_1} = \frac{1}{\tau_S} + \frac{1}{\tau_e} \\ &= \Big[ -\tau_1\,e^{-t/\tau_1} \Big]_{\tau_H}^{\tau_m} \\ &= \tau_1 \left[ e^{-\tau_H/\tau_1} - e^{-\tau_m/\tau_1} \right] \quad . \end{aligned}$$

Similarly

$$I_2 = -\int_{\tau_H}^{\tau_m} e^{-\tau_m/\tau_S} \cdot e^{-t/\tau_R}\,dt$$

$$= -\left[-\tau_R\, e^{-\tau_m/\tau_S} \cdot e^{-t/\tau_R}\right]_{\tau_H}^{\tau_m}$$

$$= \tau_R\left(e^{-\tau_m/\tau_1} - e^{-(\tau_H/\tau_R+\tau_m/\tau_S)}\right) .$$

Thus

$$R = \frac{I_1 + I_2}{\tau_S}$$

$$= \frac{\tau_1}{\tau_S}\left[e^{-\tau_H/\tau_1} - e^{-\tau_m/\tau_1}\right] + \frac{\tau_R}{\tau_S}\left[e^{-\frac{\tau_m}{\tau_1}} - e^{-(\frac{\tau_H}{\tau_R} + \frac{\tau_m}{\tau_S})}\right] .$$

Substituting

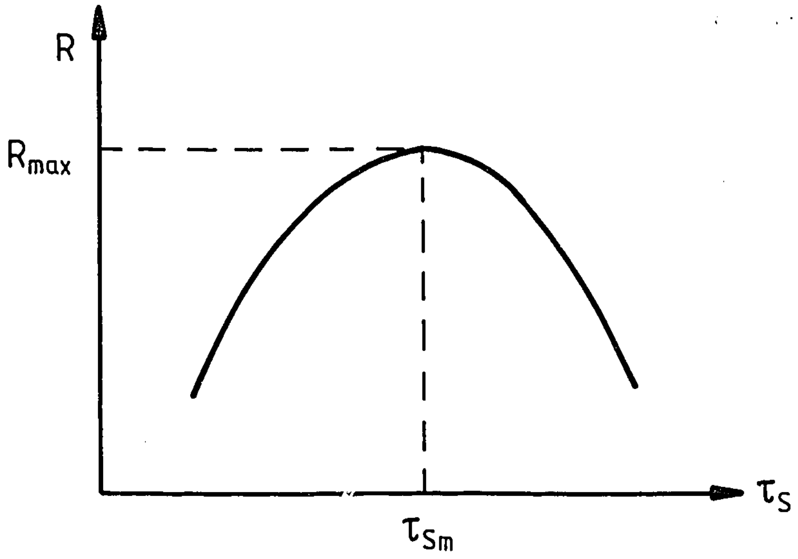
$$\frac{1}{\tau_1} = \frac{1}{\tau_S} + \frac{1}{\tau_R}$$

the expression can be rewritten to

$$R = e^{-\frac{\tau_m(\tau_R+\tau_S)}{\tau_R\,\tau_S}} \cdot \left\{-\left[\frac{\tau_R}{\tau_R+\tau_S}\right] + \frac{\tau_R}{\tau_S}\right\} + e^{-\frac{\tau_H(\tau_R+\tau_S)}{\tau_R\,\tau_S}}$$

$$\cdot \left\{\frac{\tau_R}{\tau_R+\tau_S}\right\} - e^{-\frac{(\tau_H\tau_S+\tau_R\tau_m)}{\tau_R\,\tau_S}} \cdot \left\{\frac{\tau_R}{\tau_S}\right\} .$$

Thus, solving for R in terms of $\tau_R$ and $\tau_S$ fixed to a value, with $\tau_H$ = holding time also fixed to a value and $\tau_m = 2.06\,\tau_R$ then R will maximise as shown diagrammatically:



Then, by plotting the value $\tau_{Sm}$ *v.* $\tau_S$ a correction curve for the exponential correlation can be obtained.

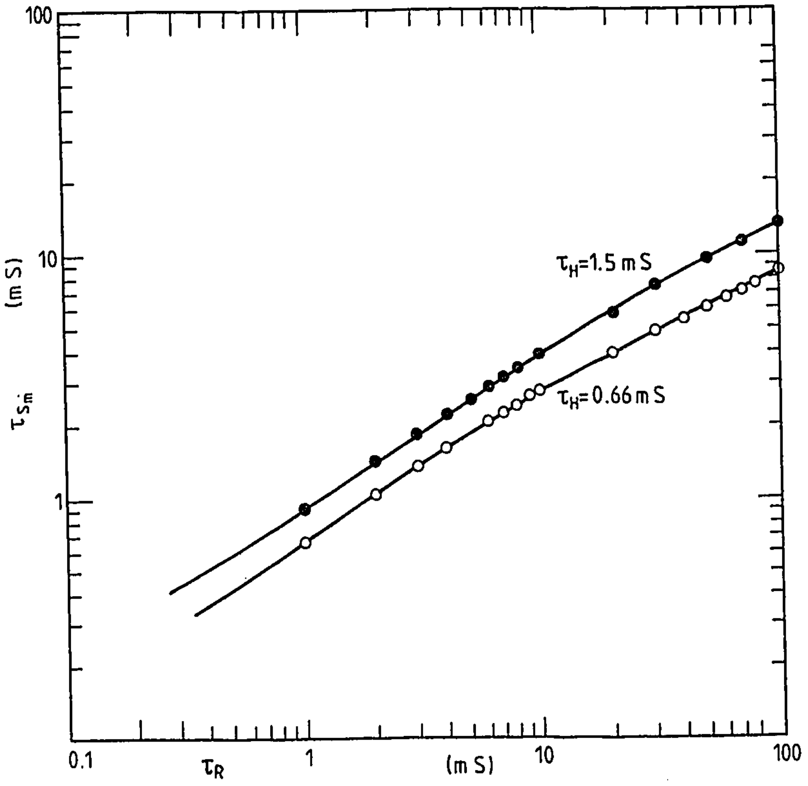


Figure A1 Correction curve for the exponential correlator for the parameters used in this report (where $\tau_H = 0.66$ ms and $\tau_m = 2.06\,\tau_R$).

The value of $\tau_{Sm}$ (for a particular value of $\tau_R$) can now be used for trap energy calculations in the relationship $\ell n\, \tau_{Sm}$ = constant + $\frac{\Delta E}{kT}$.