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AUSTRALIAN NUCLEAR SCIENCE AND TECHNOLOGY ORGANISATION

LUCAS HEIGHTS RESEARCH LABORATORIES

NEUTRON TRANSMUTATION DOPING OF GALLIUM ARSENIDE

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D. ALEXIEV

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ABSTRACT

Neutron transmutation doping (NTD) was studied as a means of compensating p-type Cd-doped GaAs. By introducing specific donor concentrations, the net acceptor level was measured and showed a progressive reduction. The NTD constant K = 0.32 donor atoms.cm^3 per n.cm^2 was also measured. Radiation damage caused by neutron bombardment was annealed and no additional traps were generated.

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ANNEALING; CADMIUM; CRYSTAL DOPING; GALLIUM ARSENIDES; NEUTRON FLUX; NEUTRONS; P-TYPE CONDUCTORS; TRANSMUTATION

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1. INTRODUCTION

The neutron transmutation doping (NTD) of semiconductor material was first demonstrated by Cleland *et al.* [1950]. They showed that a neutron flux can produce a homogeneous distribution of dopants in semiconductor materials. This work was continued by others [Colin 1963, Cuevas 1967] and is now routinely used in the commercial doping of silicon. In Si only ^{30}Si, one of the three naturally occurring isotopes, present at a concentration level of about 3.1% and homogeneously distributed, is used to produce phosphorus. Phosphorus-31 is stable and acts as a donor in Si when it is situated in a substitutional lattice site. However, this changes after neutron irradiation, so the Si has to be annealed [Lawson *et al.* 1985] to remove induced damage and relocate the ^{31}P into a substitutional site.

Neutron transmutation doping of GaAs was first studied by Mirianashvili *et al.* [1971] who demonstrated that an efficiency of the order of 10^3 times higher than in Si-neutron transmutation doping (Si-NTD), can be achieved. Gallium arsenide contains three naturally occurring isotopes which act in the transmutation doping process:

Transmutation Reaction of GaAs	Capture Cross Section for Thermal Neutrons (barn)	Half-life	Natural Abundance (%)
$^{69}Ga(n,\gamma)\,^{70}Ga \xrightarrow{\beta} {}^{70}Ge$	1.68	21 min	60
$^{71}Ga(n,\gamma)\,^{72}Ga \xrightarrow{\beta} {}^{72}Ge$	4.86	14 h	40
$^{75}As(n,\gamma)\,^{76}As \xrightarrow{\beta} {}^{76}Se$	4.30	26 h	100

If all the stable isotopes of Ge and Se are located on a Ga and As site, then each of them will act as shallow donors. Vesaghi [1982] expressed the efficiency of the doping process under this condition as

$$N_D = K \phi t \ , \quad \text{with } K = 0.16 \ ,$$

where ϕ is the thermal flux in n cm^{-2} s^{-1}, t is the time exposed to the neutron flux, K is the NTD constant, and N_D is the concentration of the donor.

As with Si-NTD, transmuted atoms in GaAs are not in their original locations and are displaced into an interstitial position because of the recoil of a γ-ray and a β-particle which the isotope emits to reach ground state. This nuclear reaction leads to a considerable concentration of defects, consequently there are deep levels which render the material semi-insulating. As with Si irradiation, this defect damage can be reduced by thermal annealing. For bulk GaAs, annealing temperatures are in the range 800 to 900°C for one hour, and 600°C is frequently used for epitaxial wafers. Vesaghi [1982] suggested that the higher annealing temperature required for bulk GaAs is associated with a high concentration of defects and impurities which may act as binding sites for the transmuted atoms.

The need for higher annealing temperatures inevitably creates new problems such as out-diffusion of As and possible contamination of the GaAs with common metallic impurities, particularly Cu, from the quartz annealing tube used in the furnace. To avoid this detrimental effect, the GaAs can be encapsulated in phosphosilicate glass [Mathur *et al.* 1985] or by some other means [Lee 1985]. Encapsulants can act as getters to fast diffusants and modify the residual impurity in the solid phase. For this reason, the annealing-encapsulating process has to be examined as a separate entity. In addition, this process often gives rise to the appearance of low-resistivity degraded layers at the surface, as was noted by Boltaks *et al.* [1983]. However, there is evidence that an overpressure of arsenic vapour can reduce or even prevent the formation of such layers.

Recent studies of deep centres in NTD GaAs have revealed that dominant antisite defects are formed. Kol'chenko *et al.* [1984] and Schneider *et al.* [1982] both found an As_{Ga} defect, identified by Kol'chenko *et al.* as a main electron trap and labelled END, which is similar to the electron trap EL2 usually observed in bulk and epitaxial film grown by vapour phase methods. Some electric field dependence was also noted by Kol'chenko. It is also of concern that this END defect could not be reduced with annealing below 4×10^{15} cm^{-3}, some three orders below the net carrier densities of the material.

The goal of the present work is to counter-dope p-type Cd-doped Horizontal Bridgman (HB) GaAs with stable transmuted isotopes of Ge and Se to produce an n-type material with a carefully controlled N_D of the order of 10^{13} to 10^{14} cm^{-3}. The initial material is a conductor rather than a semi-insulator, therefore it can be easily characterised. The procedure involves annealing with a getter before and after NTD.

2. EXPERIMENTAL

A section of p-type Cd-doped (HB) GaAs was obtained from Mining and Chemical Products (MCP), UK. The material was prepared according to accepted procedures. Briefly, a wafer was cut with a wire saw into 7 mm^2 sections. After lapping on 1200 grit paper, the GaAs was polished on a lapping cloth in a 1500 grade metallurgical paste. After washing in an ultrasonic cleaner, the GaAs was degreased in xylene, washed in methanol, then washed again in 18 MΩ water. Etching was then performed in a warm (30 to 40°C) solution of $3H_2SO_4$:$1H_2O$:$1H_2O_2$ for four minutes. The resulting surface had a mirror finish and rounded edges.

An n-type liquid-encapsulated Czochralski (LEC) semi-insulating wafer was similarly prepared. The aim was to anneal-getter the material under a flux of Ga In and revert the n-type GaAs to p-type for further controlled NTD experiments, which would only be possible, if the residual donor impurity was highly mobile and thereby gettered out of the solid.

A freshly etched sample of GaAs was first encapsulated in a type 306 glass forming solution, obtained from Emulsitone Co., New Jersey. The solution was applied with an eye-dropper and only a single drop was deposited on to the sample which was spun at 2000 rev min^{-1}. The sample was then heated in air (manufacturer's recommendation) at 200°C for 15 minutes. In this way, a layer of silica-film was deposited at a thickness of 800 to 1000 A (80 to 100 nm).

The silica-film encapsulated GaAs was then heated at 850°C in an atmosphere of 2% H_2+argon. **Figure 1**, adapted from Mueller *et al.* [1980], shows resistivity (ρ) as a function of annealing temperature T; ρ can be taken as a measure of lattice defect density in particular numbers of As and Ga interstitials present after the transmutation process. The graph shows that annealing of the defects starts at about 400°C and is completed at 700°C. Annealing times used by Mueller *et al.* were 30 minutes. For a higher degree of confidence, 850°C was used throughout an annealing run.

Since the objective of encapsulation was also to getter the material, annealing periods of 44 hours were used. The silica-film detached itself from the GaAs surface and formed small slivers. A variation of annealing times did not change this situation, so the use of silica film as an encapsulant was abandoned.

The following method of encapsulation was more successful and hence adopted throughout the experimental work. A Ga In solution was again applied to a freshly etched surface of GaAs which was then sandwiched between Si wafers, as shown in **figure 2**. The Si wafers prevented the Ga In from coagulating and completely covered the GaAs sample throughout the annealing-gettering period.

Since Ga is a solvent for GaAs at high temperatures, some recrystallisation was noted after the run; thus each sample had to be reprocessed in the normal fashion, *i.e.* lapping, polishing and then etching.

The first group of anneal-gettered samples were LEC semi-insulating GaAs. The material was characterised using optical deep level transient spectroscopy (DLTS) techniques [Alexiev and Tavendale 1984] before transmutation and found to be dominated by the hole trap spectra shown in **figure 3**. After 120 hours of anneal-gettering, the material remained n-type but had altered to low resistivity. The annealed GaAs proved to have good surface barrier diode characteristics, with a maximum V_R at 2.0 volts.

Carrier concentration [N(x)] profiles were made for each sample using capacitance-voltage (C-V) measurements. N(x) was of the order of 0.92 to 3.6×10^{18} cm^{-3}. A capacitance DLTS spectrum (**figure 4**) revealed that the GaAs now had two deep donor and two shallow acceptor states. The Arrhenius plot in **figure 5** gives the following trap energies:

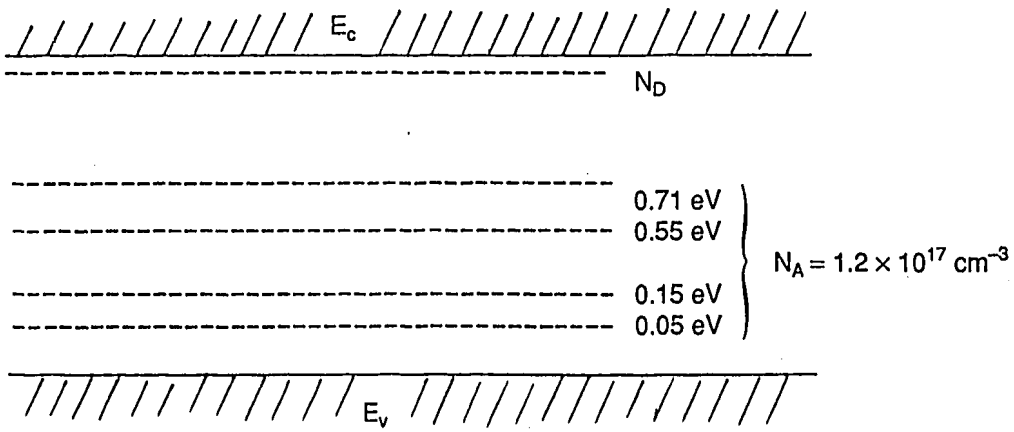
- Deep electron trap labelled e_1 = 1.14 eV.
- Deep electron trap labelled e_2 = 1.19 eV.
- Shallow hole trap labelled h_a = 0.24 eV.
- Second shallow hole trap could not be resolved.

It is interesting to note that previous hole traps found in the semi-insulating state of this material have been removed. There are two possible reasons. First, as indicated by the change of resistivity, the material has lost a compensating impurity such as SI owing to the getter action of the Ga In. Second, and more likely, there has been a redistribution of As vacancies in the solid phase at high annealing temperatures. No further work was done on this material since the objective was to convert it to p-type for NTD experimentation.

The p-type Cd-doped GaAs was treated similarly. The net impurity concentration [N(x)] remained at 1.2×10^{17} cm^{-3} throughout the anneal-getter cycles; the p-type polarity of the sample also did not change. The DLTS spectrum shown in **figure 6** reveals shallow and deep hole trap centres with some marginal reduction in intensity after several annealing cycles. It is also noted that a change in field strength (V_R) produces some dependence on one of the deeper hole traps. In **figure 7**, a mean-square fit for the Arrhenius plot gives the following trap energies:

- deep hole trap labelled h_1 = 0.71 eV.
- deep hole trap labelled h_2 = 0.55 eV.
- shallow hole trap labelled h_3 = 0.15 eV.
- shallow hole trap labelled h_4 = 0.05 eV (estimated, possibly carbon known to be at 0.026 eV).

The electronic levels of the p-type Cd-doped starting material can be represented schematically:



The group of GaAs samples selected for neutron transmutation doping were placed inside an aluminium canister which in turn was placed into 'Rabbit' carrier No. 1 and located 2.5 cm from the core tank of the Lucas Heights 100 kW research reactor Moata. The neutron flux at that position is $\phi = 7.5 \times 10^{11}$ n cm^{-2} s^{-1}.

The first group of GaAs samples was irradiated for 2.5 hours at 7.5×10^{11} n cm^{-2} s^{-1} producing 2×10^{16} donor atoms cm^{-3} and altering the residual acceptor level from 1.2 to 1.0×10^{17} atoms cm^{-3}. The GaAs samples thus remained p-type.

It was of interest to examine the residual γ-ray spectrum, using a 35 cm^3 Ge(Li) detector, ten days after the sample was removed from the reactor. The γ-ray spectrum accumulated over 4000 s was not unexpected except for a 411.9 keV γ-line identified as ^{196}Au (412 keV) which is a common contamination found in acids used in the etching process. The γ-ray spectrum is shown in **figure 8** including identification of the spectral lines.

The same group of GaAs samples was then subjected to two more irradiations with integrated fluences of 2.02×10^{16} and 3.9×10^{16} n cm^{-2}, respectively. After each irradiation, the highly radioactive GaAs samples were left for three weeks to decay to an acceptable level. The samples were then etched, annealed and gettered, etched and finally metallised as described earlier in this report. The residual acceptor level was measured and then plotted against the neutron fluences (**figure 9**).

At a neutron fluence of 2.02×10^{16} n cm^{-2}, the residual acceptor level dropped to 5.5×10^{16} cm^{-3}; however, at a fluence of 3.9×10^{16} n cm^{-2} the residual acceptor level did not progress to a near compensated state but instead assumed a value of 2.8×10^{16} atoms cm^{-3}, which was higher than expected.

A critical examination of the Moata irradiation facility suggested that a number of procedural errors could occur — first, by a variation in the neutron flux (rated at ± 5 per cent of 7.5×10^{11} n cm^{-2} s^{-1}) and second, because of the timing procedure of the irradiation of samples. It is interesting to note that such problems can be eliminated by using rhodium wire detectors and analogue current integrators with preset alarms. The neutron detector utilises the β-decay of ^{104}Rh to produce a current proportional to the neutron flux. Thus in a similar way to ϕ *v.* N(x), charge *v.* N(x) calibration constants could be obtained reducing the NTD process to a routine level by eliminating progressive N_A or N_D measurement and fluence readjustment.

3. SUMMARY AND CONCLUSIONS

When investigating the NTD of GaAs, it is essential that the starting material is p-type so that a controlled compensation to n-type can be made. For this reason, p-type Cd-doped material was used. The material was conductive rather than semi-insulating and could readily be characterised using C-V and DLTS techniques.

It was found that the material had several acceptor levels located at about $E_v + 0.71$ eV, $E_v + 0.55$ eV, $E_v + 0.15$ eV, $E_v + 0.05$ eV. The total concentration of the residual acceptor level was found to be 1.2×10^{17} impurity atoms cm^{-3}. When donors were added in a controlled fashion by the NTD process, a progressive compensation was noted in the acceptor level. The added donor concentration was measured after annealing; it agreed roughly with other published results. The annealed control samples showed no substantial change to the trap spectra of the original material. Deep level transient spectra taken after irradiation/annealing also remained unaltered, thus no new hole or electron traps were introduced by the NTD process.

In summary, the neutron transmutation doping method has the advantage of being predictable, controllable and uniform, with none of the problems of segregation when a dopant is introduced into a melt or by high temperature diffusion in a solid. It is a one-way process, whereby p-type can go to n-type and finally to low resistivity n-type.

However, based on the results obtained from the Moata irradiation facility (**figure 9**), the NTD constant can be calculated as K = 0.32, which is comparable to the published value of K = 0.16 [Vesaghi 1982]. This constant can only be taken as a guide for the NTD fluence estimate. When using a different reactor facility, a new NTD constant would have to be derived.

When examining the (annealed) NTD GaAs samples for induced new defect states using DLTS, it was found that no new traps were generated in addition to the trap spectra categorised earlier.

4. ACKNOWLEDGEMENTS

I would like to thank Dr A.J. Tavendale for supporting this project. I wish also to thank Mr A.A. Williams for carrying out the deep level transient spectroscopy and Mr T. Wall for irradiating the samples.

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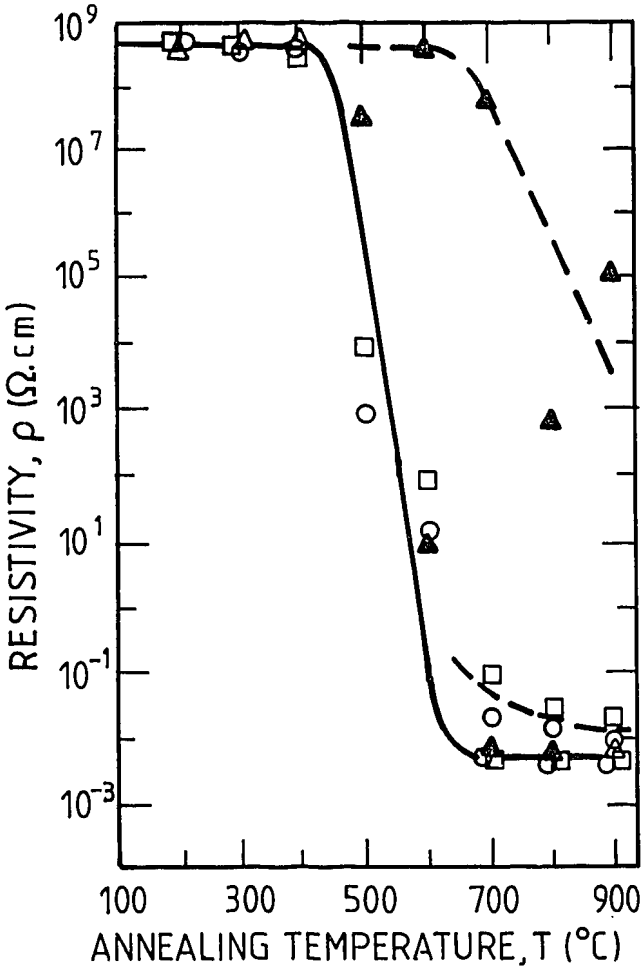

Figure 1 Resistivity (ρ) as a function of the annealing temperature T (annealing time 30 min). Starting material: No. 1 O, No. 2 □, and No. 3 Δ. Transmutation doping: 1×10^{17} cm^{-3} (dashed line), 5×10^{17} cm^{-3} (solid line). (Redrawn from Mueller *et al.* [1980])

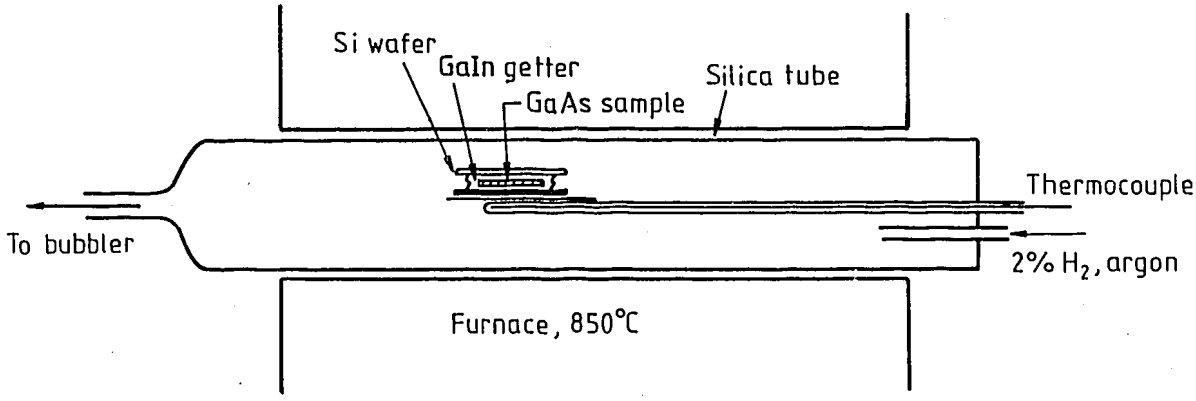

Figure 2 Anneal-getter arrangement of GaAs.

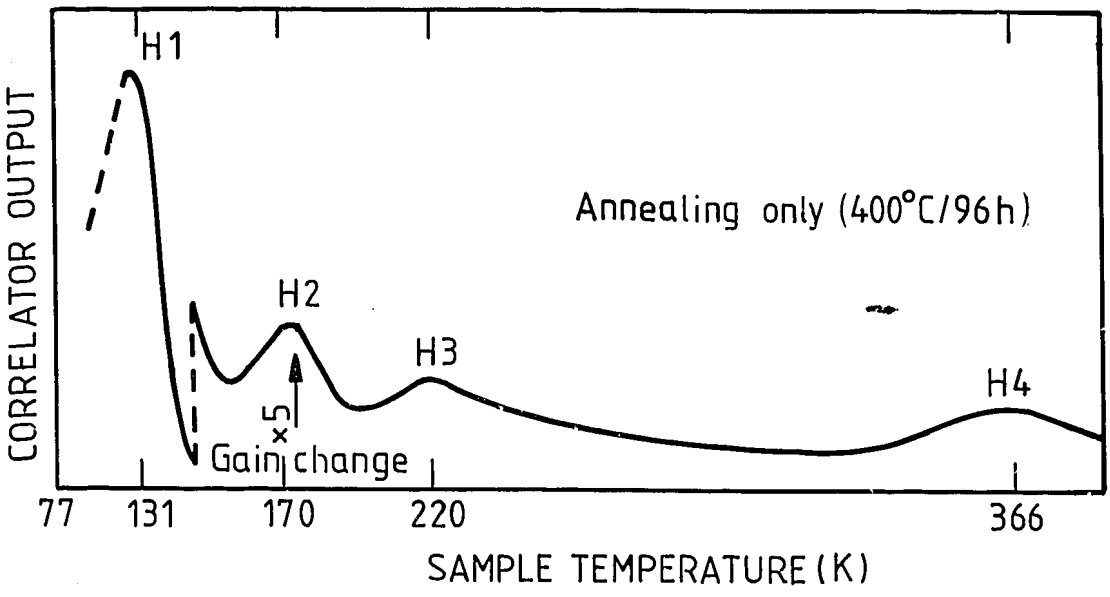

Figure 3 Optical deep level transient spectroscopy.
Hole trap spectra of n-type semi-insulating GaAs.

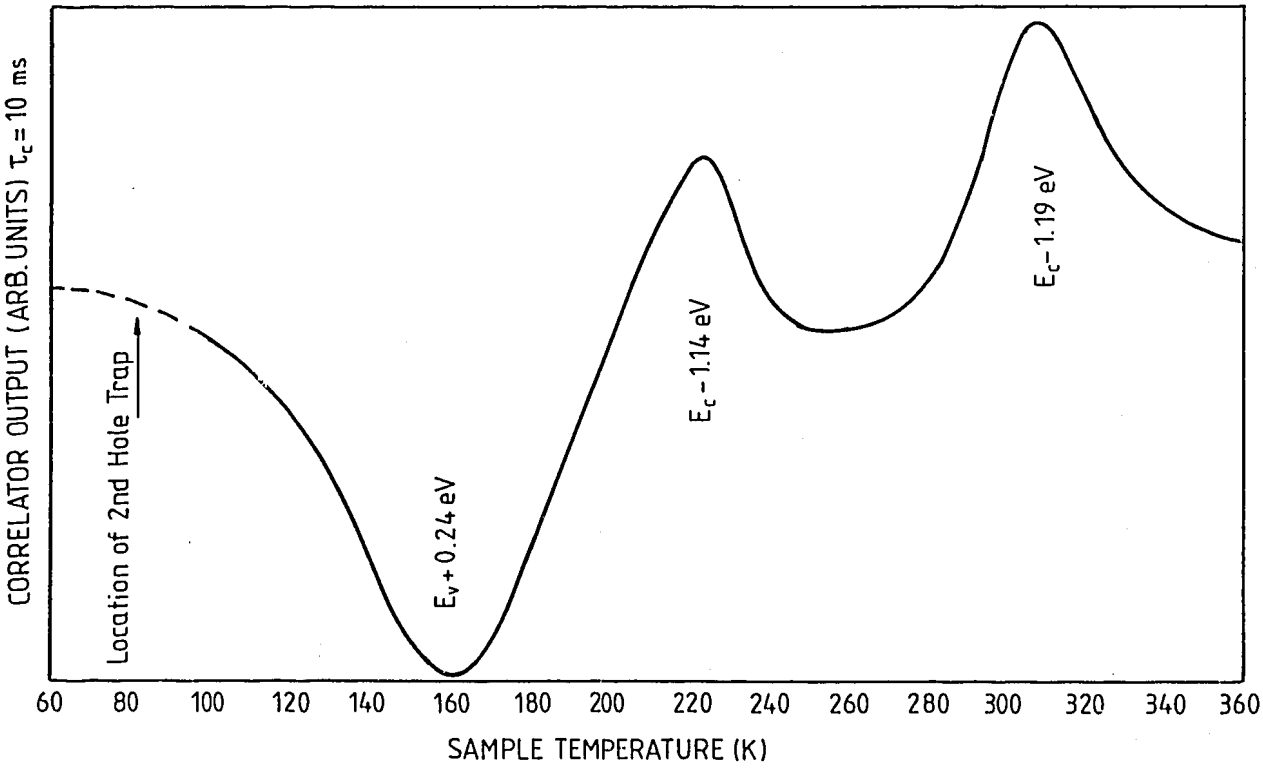

Figure 4 Anneal-gettering of n-type (LEC) semi-insulating GaAs produced n-type low resistivity material with a new electron-hole trap spectrum

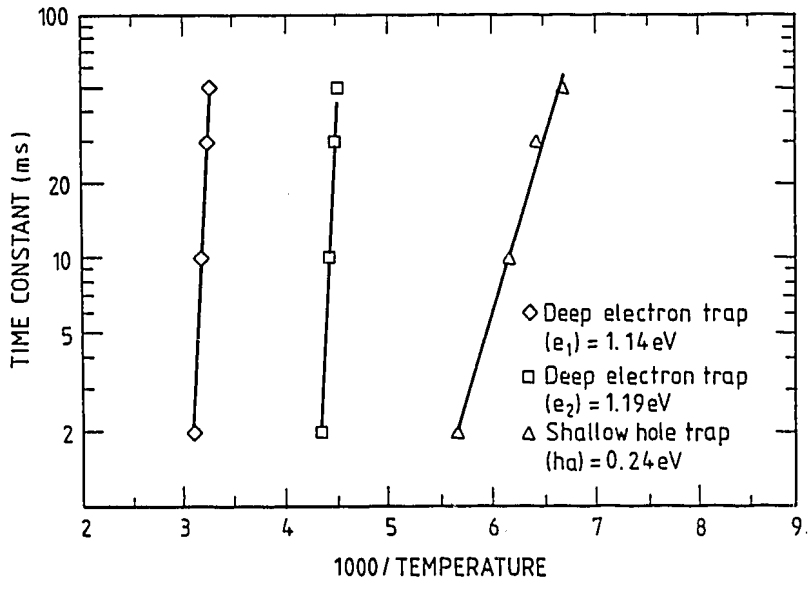

Figure 5 An Arrhenius plot of the (anneal-getter) n-type low resistivity GaAs. Used to determine the electron-hole trap energies.

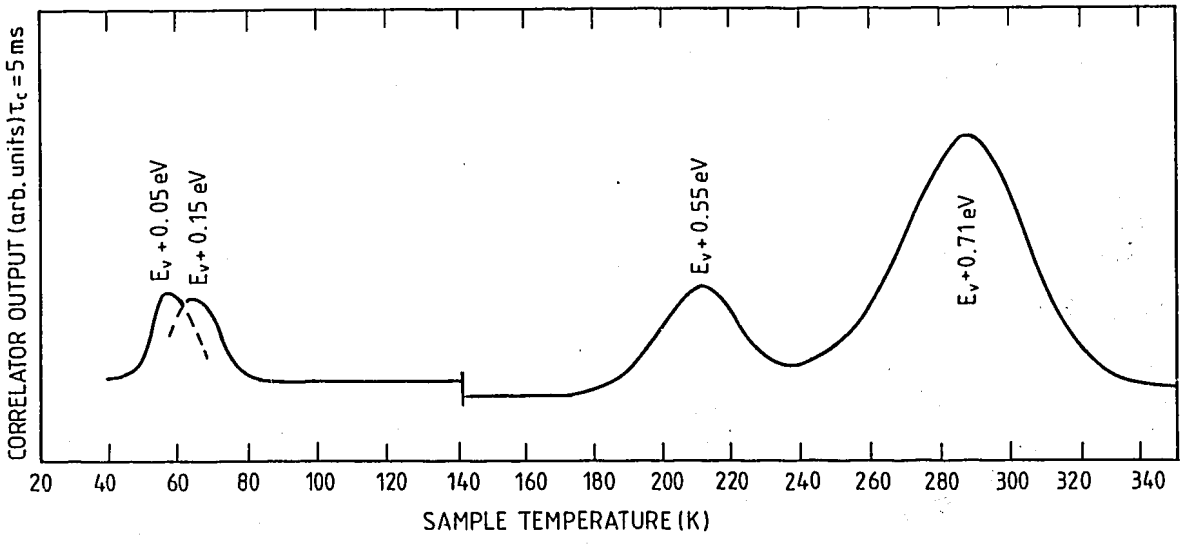

Figure 6 DLTS hole trap spectrum of p-type (Cd-doped) GaAs before NTD irradiation

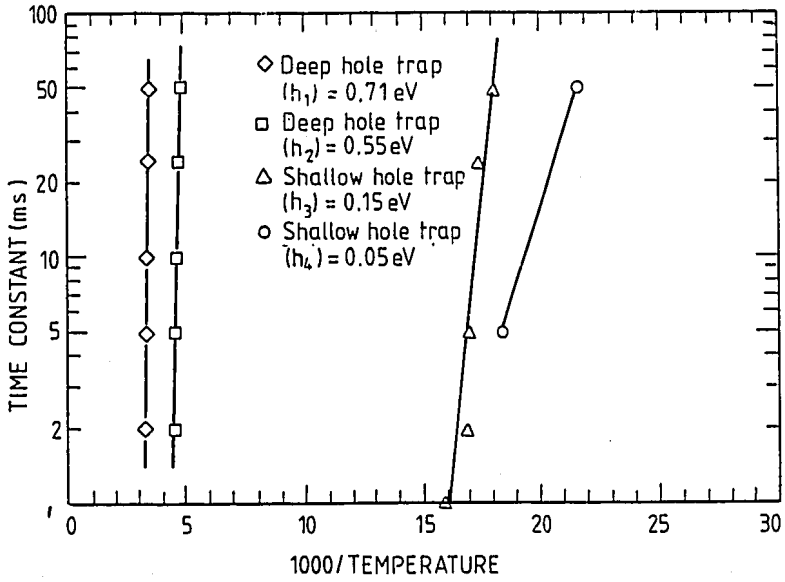

Figure 7 Arrhenius plot used to determine hole trap energies of p-type (Cd-doped) GaAs

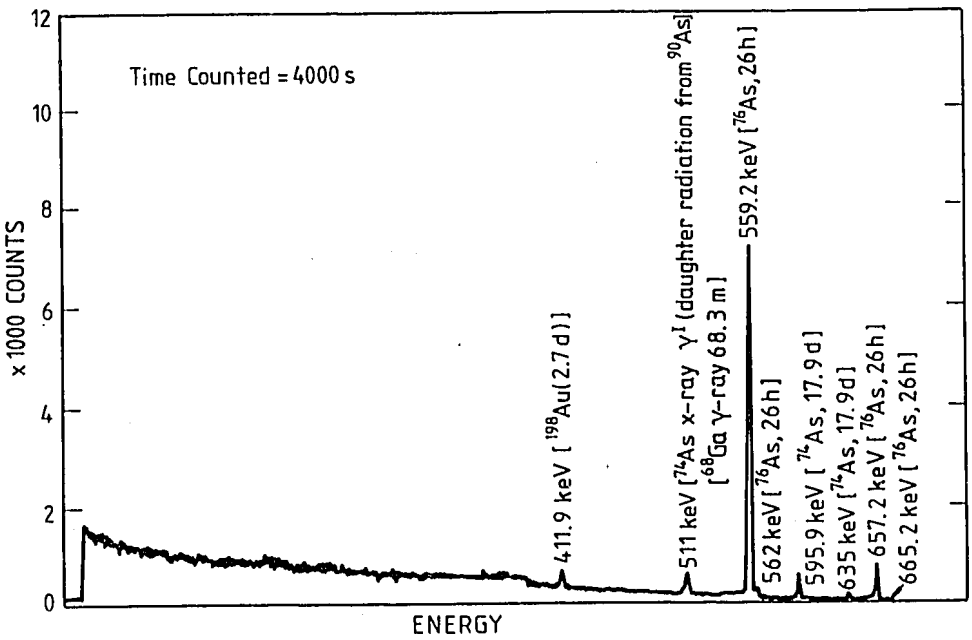

Figure 8 Residual γ-ray spectrum taken ten days after neutron transmutation doping irradiation of p-type (Cd-doped) GaAs. Of particular interest is the 411.9 keV ^{198}Au line, a common contamination from acid etchants.

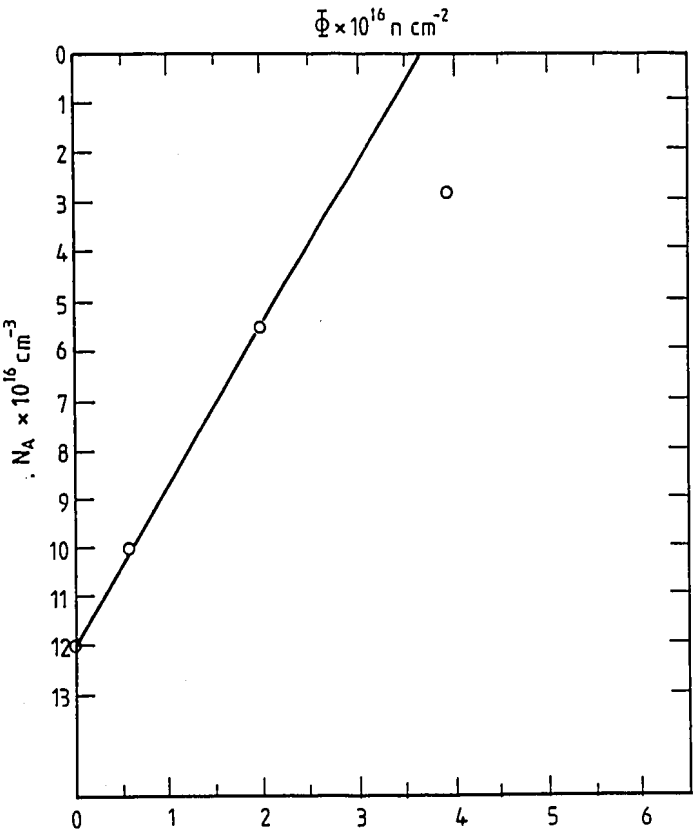

Figure 9 The graph shows net acceptor (N_A) concentration *v.* neutron fluence (ϕ). The NTD process was used at the Moata reactor, Lucas Heights. Material used for the NTD experiments is p-type (Cd-doped) GaAs.