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Doping Gradients in Layers of Gallium Phosphide Grown by Liquid Epitaxy

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Layers of epitaxial gallium phosphide doped with either tellurium, sulphur or zinc over the range 10^{16} to 10^{18} cm^{-3} have been grown from gallium solution using a vertical dipping system. These layers of thickness 60 to 80 μm have been produced on the (100) and (111)B faces of gallium phosphide single crystal substrates at high growth rates. Doping gradients have been investigated by a Schottky barrier technique over an angle lapped region of the grown slice, measuring the capacitance voltage characteristics of the individual barriers. Significant changes in doping level have been observed throughout the thickness of the layers and these are related to the variation of distribution coefficient, the losses of impurity from the system and the presence of competing background impurity systems.

1. Introduction

It has been reported previously [1, 2] that the fabrication of high efficiency gallium phosphide light emitting diodes, red and green, has been best achieved by a p/n structure where both layers have been grown from solution. Efforts to improve the diode efficiencies have led to a need for greater control and understanding of the processes occurring during growth, particularly with respect to the impurity concentration profiles in the crystal and hence the control of the electrical characteristics of the material. Earlier workers characterised their material by Hall effect measurements but except for the case where there is an absence of doping gradient this result can be misleading giving an answer tending towards the highest value in the layer regardless of its position. In the majority of cases of epitaxial growth of gallium phosphide, large doping gradients exist unless particular techniques have been adopted.

Although data has been published on the distribution coefficient of various important electrically active impurities in gallium phosphide, these are mostly for growth from a stoichiometric melt at its melting point [3] or for growth from the vapour phase by halide transport [4]. Little information is available on the doping characteristics of the various important elements when the crystals are grown from a Ga rich melt. To treat the problem theoretically in any detail, it would be necessary to simultaneously consider fluid flow in the melt, solute concentration gradients, undercooling at the solid liquid interface, and other interface phenomena involving absorption, nucleation, surface diffusion, etc. The effect of impurities on each of these parameters would also have to be considered. In view of the present lack of basic data, this would seem impracticable. Experimentally however, much useful information can be collected and hence we have investigated the doping gradients in our liquid epitaxy system for undoped, sulphur, tellurium, zinc and zinc/oxygen doped material using a Schottky barrier technique and have subsequently made efforts to reduce them.

2. Experimental

2.1. Liquid Epitaxy Growth Process

The first liquid epitaxy layers were grown from gallium solution using the horizontal tipper technique [5]. In our laboratories the majority of the work has been concentrated on the vertical dipping system, illustrated in fig. 1 [6, 7], which has proved to be a more easily controlled system readily lending itself to scaling up for the processing of large substrate areas.

The quartz reaction vessel, surrounded by a wire resistance furnace and gold plated reflector, was carefully cleaned in silica cleaning fluid

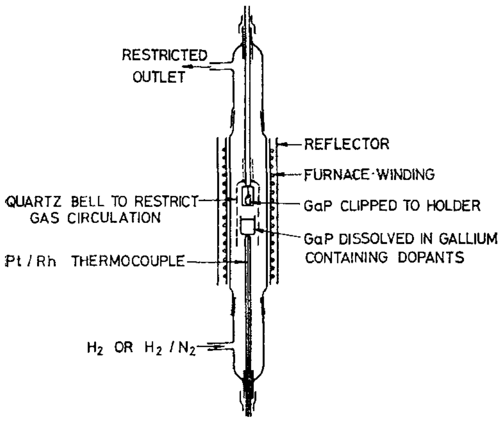

Figure 1 Liquid epitaxy apparatus.

(1:7:12, $HF:HNO_3H_2O$) and thoroughly rinsed with de-ionised water prior to use. The furnace profile was such that the melt was situated in a region where the temperature increased from the bottom to the top of the melt by approximately 10° C thus reducing the convection effects which could lead to severe instability problems in melts greater than 1 cm high. A melt consisting of an 8.4 mole % solution of polycrystalline gallium phosphide (9^5 purity) in gallium was held in the quartz crucible as shown and the substrates were pinned to the holder with 1 mm diameter quartz rod. Experiments were conducted in which a vitreous carbon crucible was substituted together with a carbon coated holder in an attempt to reduce the background silicon contamination. The electron mobilities for the gallium phosphide layers grown using the carbon crucible and substrate holder were consistently higher than those for layers grown in the original apparatus, and although the back-ground impurity concentration did not decrease, this modification was adopted as general practice, except for zinc/oxygen doped layers. No evidence of carbon contamination was found in the material.

Doping of the grown layers was achieved by the addition of the elemental dopants (9^5 purity) directly to the melt except in the case of oxygen doping where powdered β form Ga_2O_3 was added. The majority of investigations were concerned with typical doping levels of the order of 10^{17} to 10^{18} cm^{-3}, appreciably higher than the residual impurity level but not so high that precipitation would cause problems.

The substrates used were either (100) or (111)B oriented slices cut from gallium phosphide ingots grown by the liquid encapsulated Czochralski technique [8] or were high resistivity ($\rho > 10^3$ Ω cm) slices grown by the halide transport vapour deposition technique [4]. Prior to use, they were lapped, polished with 1 μm, then $\frac{1}{4}$ μm paste, degreased, etched in 50% aqua regia and finally rinsed in double de-ionised water. For good quality epitaxial growth, a low initial super saturation was to be preferred, but it was also essential to keep any back-etching of the substrate *in situ* to a controlled minimum if consistent doping profiles were to be obtained. The melt was taken up to 1040° C in an atmosphere of palladium diffused hydrogen and held at that temperature for 10 min to allow all the polycrystalline gallium phosphide to completely dissolve. During this period the substrates were lowered to a position just above the melt surface. After a further 4 min, the substrates were dipped into the melt, back-etched by increasing the melt temperature and then cooled at a rate which could be varied from 0.1 to 10° C/min until 910° C was reached, at which point the substrates were removed from the melt to a colder region of the growth tube. A facility for stirring the substrates at rates of the order 5 rev/min was included in the apparatus. For zinc and zinc/oxygen doped layers, the substrates were not withdrawn at 910° C but left in the melt down to 25° C. These conditions gave smooth layers approximately 60 μm thick exhibiting microscopic (1 μm) undulations commonly observed on liquid epitaxially grown surfaces. Any growths with gallium inclusions either in the layer or at the layer/substrate interface were discarded as unsuitable for further work. If the growth had continued at this rapid rate the onset of constitutional supercooling, caused by a build-up of solute at the interface depressing the liquidus temperature, would have caused the complete break-up of the crystal structure; but for growth thicknesses < 100 μm this did not occur.

2.2. Measurement Technique

For the range of impurities used, the only practicable methods of accurately measuring the doping levels in narrow regions are based on electrical techniques. Of these it has been found that a Schottky diode method [9] enables rapid measurements to be taken with a high degree of accuracy.

Because of the small penetration of the Schottky diode depletion region for the doping levels used, in order to obtain values for the whole of the grown region it is necessary to angle lap the layer and evaporate a matrix of circular gold barriers over the bevelled area. This structure enables a series of discrete values of carrier concentration to be determined at equal intervals below the semiconductor surface. If high accuracy is to be obtained, the lateral variation of doping level across the slice must be small in comparison to the vertical change and it must also be possible to use the standard relationship to determine carrier concentration values from the C-V characteristics, namely:

$$\frac{1}{C^2} = \frac{2(V_d - V)}{q\,\epsilon\,n}$$

where q is the electronic charge, ϵ the absolute permittivity of the semiconductor, n the carrier concentration, V_d the barrier diffusion voltage, V the applied voltage and C the capacitance per unit area.

The first condition was found to be met in almost all circumstances and is true for the data presented in this paper. The second requirement was met by examining the I-V characteristic of the diodes. If the value of n in:

$$I \propto \exp\left(\frac{qV}{nkT}\right)$$

was greater than 1.10 the diode was assumed to be non-ideal due to interfacial layers or surface states and was not used in the measurements.

The capacitance measurements were made using a 1 MHz autobalance bridge, each barrier being contacted in turn by a gold wire probe. The largest error was in the determination of diode area but the absolute error of the measurement was estimated to be not more than ± 10% with a relative error of not more than ± 5%.

The method does, however, determine the free carrier concentration which is not necessarily the impurity concentration. The measured value normally is equal to the net value of electrically active impurity concentration, that is it represents the difference between ionised donor and acceptor concentrations. Previous work has related the individual values of donor and acceptor concentration to the total impurity concentration by radiotracer techniques [3]. This discrepancy can be identified in our results and is discussed later.

3. Results

Both Hall and Schottky measurements showed all the undoped layers to be n-type. Low temperature Hall measurements and more recent cathodoluminescent studies have indicated silicon to be the predominant background impurity with small amounts of sulphur also present. This corresponds to observations reported previously [10, 11] which showed that with similar apparatus and techniques to those described in this paper the total atomic Si content ($k_0 \simeq 0.6$) would be approximately 5×10^{17} cm^{-3} for layers grown on (111) substrates. The value of $N_D - N_A$ calculated from the capacitance data is plotted in fig. 2, with respect to position in the grown layer. This position was measured relative to the top surface of the epitaxy layer, that is, the last grown surface. It can be seen that there is a consistent increase in the net carrier concentration from first grown region to the surface by a factor of approximately six. By comparison with the growth schedule these initial and surface values correspond to temperatures of 1040 and 910° C respectively.

Fig. 2 also shows the marked anisotropy of the distribution coefficient. This was first reported by Hall [12] who suggested that the possible mechanism for the non-equilibrium amount frozen into the solid in the (111) direction was

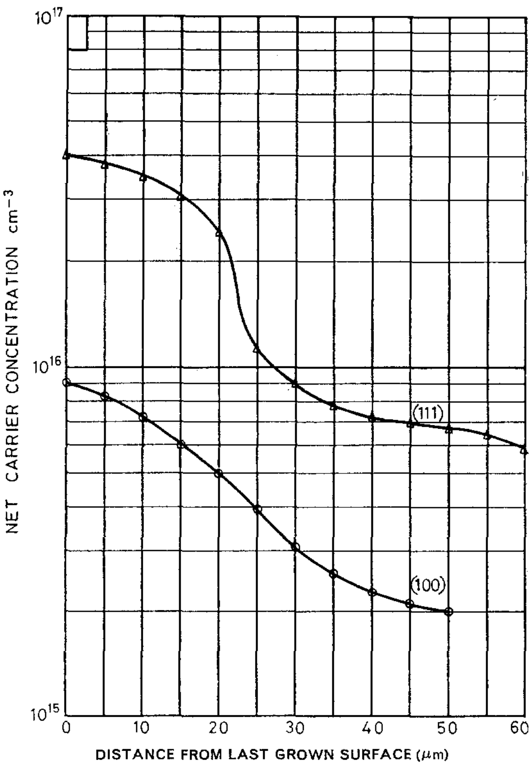

Figure 2 Doping profiles in undoped liquid epitaxial layers of GaP grown on (100) and (111) orientated substrates.

due to the interface being singular and thus requiring the nucleation of growth steps to advance. The lateral velocity of these steps due to surface diffusion can be greater than the velocity normal to the solid/liquid interface, namely the growth velocity [13] and consequently this could account for the increased value of k (1 1 1).

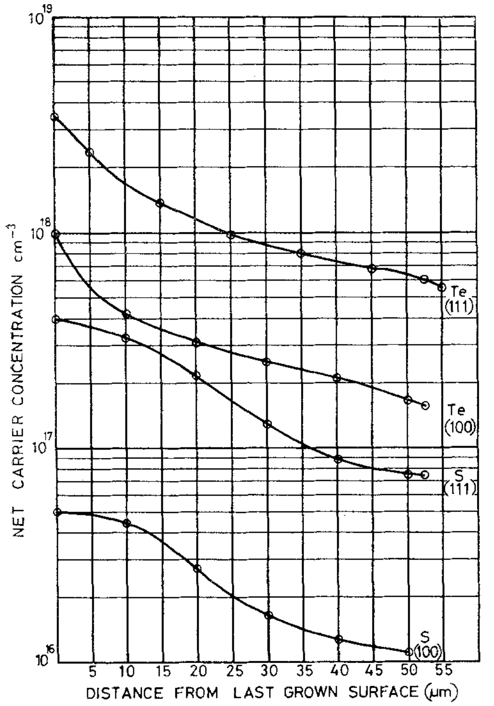

Figure 3 Doping profiles in Te and S doped liquid epitaxial layers of GaP grown on (100) and (111) orientated substrates.

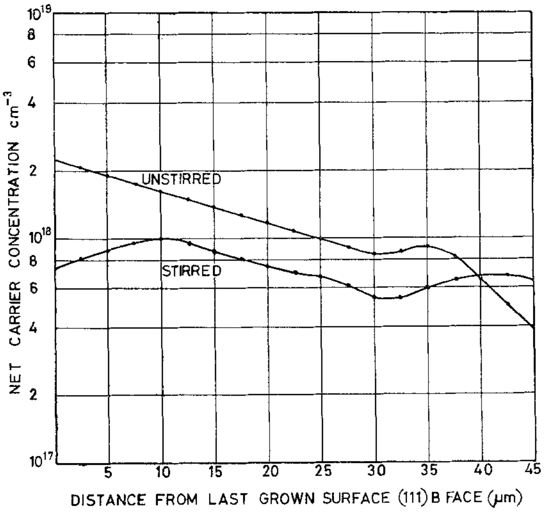

Figure 4 Doping profiles in Te doped liquid epitaxial layers of GaP grown on (1 1 1) orientated substrates showing the variation of the profiles with stirring.

The profiles for sulphur and tellurium doped samples are plotted in fig. 3. These show a similar increase in net carrier concentration from first to last grown regions as observed with the undoped samples. To obtain initial n-type concentrations of the order 2×10^{17} cm^{-3} it was necessary to add approximately 10^{-3} at. % Te or 10^{-4}% S to the melt. Losses from the melt due to evaporation were minimal as indicated by the fact that up to five consecutive runs from the same melt each gave identical profiles and almost the same initial concentration. The shapes of the profiles for each dopant type on different substrates did not differ appreciably and were consequently considered to be independent of the substrates. This meant that providing the back etch was kept to a controlled minimum compatible with good growth the profiles observed could be attributed entirely to the growth process. Each of the profiles in figs. 2 and 3 were measurements taken on layers grown from unstirred melts at the comparatively fast cooling rate of 10° C min^{-1}.

The results plotted in figs. 4 and 5 show the effect on the profiles of the introduction of mechanical stirring and the use of slower cooling rates. Suitable choice of these two parameters could reduce the difference in net carrier concentration from the initial growth to the surface to within a factor of two. The significance of these results will be discussed later.

The net carrier concentration for the zinc and zinc oxygen doped samples decreased with distance from the first grown region by a factor of at least ten, fig. 6. Problems due to evaporation losses were encountered and the melt had to be re-doped after each run. The effect on the profile of adding oxygen to the melt was negligible with just a slight drop in concentration due to compensation although the electrically active oxygen content was thought to be only 5×10^{16} cm^{-3}. More important was the effect of the residual impurity level creating a near compensated region close to the surface where the zinc concentration had dropped to below 10^{17} cm^{-3}.

4. Discussion

The theories of growth from the melt particularly with respect to normal freezing and zone melting

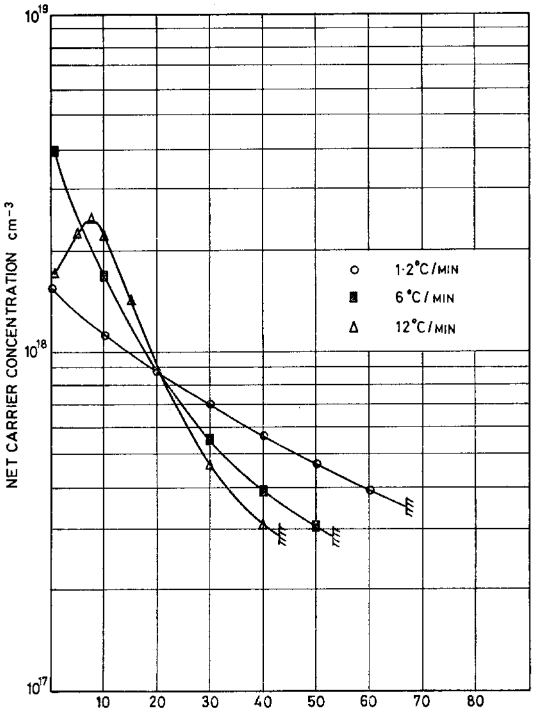

Figure 5 Doping profiles in Te doped liquid epitaxial layers of GaP grown on (111) orientated substrates showing the variation of the profiles with cooling rate.

have been discussed in great detail elsewhere [14-16]. Chemical reactions occurring at the interface of two phases depend not only on the chemical transformation itself but also on the transport of reactants or products to or from the interface. The significance of a single process depends critically upon the system under study and often upon the individual experimental conditions.

The equilibrium distribution coefficient k_0 defined as:

$$k_0 = \frac{\text{concentration in solid } (C_S)}{\text{concentration in liquid } (C_L)}$$

characterises the incorporation of impurity in a crystal when equilibrium exists between the two phases for a given temperature and, according to whether the addition of solute raises or lowers the melting point of the solvent, the value of k_0 can be less than or greater than unity. If however, crystallisation does not proceed slowly, solute atoms are rejected by the advancing solid at a greater rate than they can diffuse into the bulk of the melt where fluid flow dominates. This

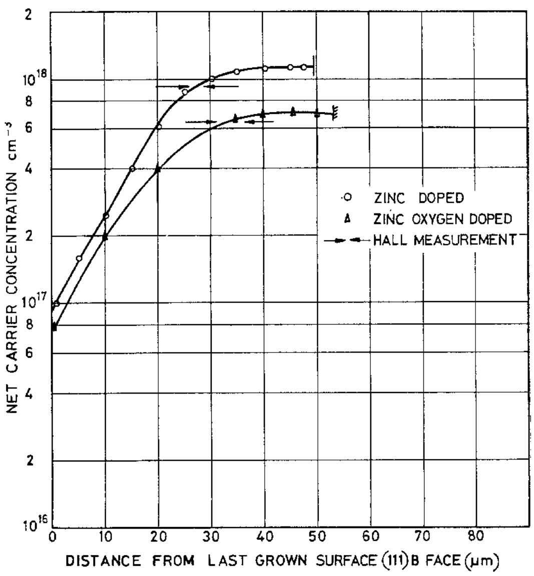

Figure 6 Doping profiles in Zn and Zn/O doped liquid epitaxial layers of GaP, grown on (111) orientated substrates.

leads to the definition of two further distribution coefficients:

$k = (C_S)/(C_L)$ for finite growth rate

$k^* = (C_S)/(C_L)_{(0)}$ for finite growth rate

Whether the flow in the liquid is laminar or turbulent there will be a region of laminar flow very close to the interface where the velocity of

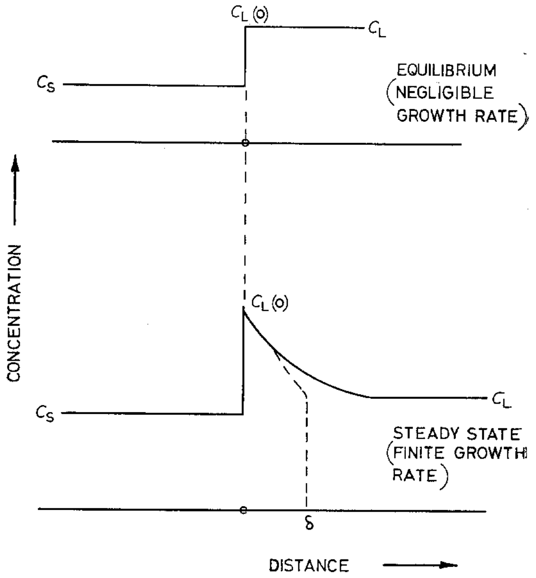

Figure 7 Solute concentration near an advancing solid-liquid interface for different conditions of crystal growth. (After Burton and Slichter.)

flow, except that velocity normal to the interface due to crystallisation, is so small that diffusion is the primary means of transport. Outside this region, width δ, transport by fluid motion can dominate. It can be shown that

$$\delta = 1.6\, D^{1/3}\, \nu^{1/6}\, \omega^{-1/2}$$

[15] where D = diffusion coefficient, ν = kinematic viscosity, and ω = angular speed of rotation and has typical values of 10^{-3} cm for a vigorously stirred melt, 10^{-1} cm for an unstirred case. In the growth of liquid epitaxy layers, the thickness of growth is approximately 50 μm or less, and hence the crystallisation occurs in a region where diffusion is the primary means of transport although changes in the fluid motion in the bulk can affect δ and hence $C_{L(0)}$.

Burton *et al* [14] have considered a one-dimensional analysis of the steady state situation by considering the conservation of solute atoms at the interface and by applying appropriate boundary conditions. They assumed that the diffusion coefficient of the solute was independent of concentration in dilute solutions, that the fluid was incompressible, and that the one-dimensional analysis was appropriate since the radial solute distribution was uniform. This simplified the continuity equation to:

$$D\frac{\mathrm{d}^2 C_X}{\mathrm{d}x^2} - V_X\frac{\mathrm{d}C_X}{\mathrm{d}x} = 0$$

where C_X is the concentration at point x V_X is the sum of the normal fluid velocity W and the growth velocity f, and D is the diffusion coefficient of the solute. This leads to the following expressions for the effective distribution coefficient in the solid.

$$k = \frac{k^*}{k^* + (1 - k^*)\exp -\Delta}$$

where $\Delta = (f\delta)/D$ = normalised growth velocity, f = linear growth rate. D = diffusion coefficient for impurity in solution. The term Δ embodies the three main factors affecting the distribution coefficient in that k depends critically on the relative magnitude of the linear growth rate and the diffusion coefficient while external factors such as stirring can affect the value of δ.

Experiments completed in our laboratories have shown that the growth rate for our specific conditions changes linearly with temperature by a factor of 5 to 6 over the temperature range concerned (1040 to 910°C) but below 915°C it decreases rapidly to zero. The rate of diffusion of the elemental impurity decreases exponentially over this range from its initial typical value of 10^{-5} cm^2 sec^{-1}. This work suggested that both the growth rate and diffusion rate could each dominate alternately during the growth cycle.

4.1. *n*-type Material

Although Saul and Hackett [17] suggested that the incorporation of tellurium in gallium phosphide was an equilibrium process and that the doping profiles observed in their liquid epitaxial layers reflected a true temperature dependence of the distribution coefficient, the results presented in this paper are to the contrary. The data obtained and presented in figs. 4 and 5, indicate that the incorporation of these dopants is kinetically controlled rather than an equilibrium process. It can be seen from figs. 3, 4 and 5, that regardless of the growth conditions used, the initial slopes of the *n*-type doping profiles are very similar. This can be explained by the fact that during the initial stages of growth, that is at the higher temperatures used, the growth rate of the liquid layer and the diffusion rates of S and Te in Ga are on the same order of magnitude and as a consequence, the dopant concentration would be independent of their diffusion rates and could therefore show a true dependence on distribution coefficient. As the temperature is lowered, the diffusion rate of the dopants tends to decrease at a much greater rate than the speed of growth and hence the incorporation of *n*-type dopants becomes diffusion controlled and as $k < 1$ a build-up of impurity occurs at the growth interface leading to an increased concentration in the solid. If growth was continued at temperatures below 910°C, then because of the rapid decrease in the speed of growth, the incorporation of dopant into the layer during this period could no longer be diffusion controlled and the concentration in the solid would be expected to reduce to that calculated from the concentration in the bulk of the liquid and the equilibrium distribution coefficient at that temperature. This has been confirmed experimentally, an example is shown in fig. 5 for the layer grown at a cooling rate of 12°C/min^{-1}.

As a result of these observations, it is reasonable to assume that only the profiles of material grown at slow cooling rates (< 1°C/min^{-1}) from a stirred melt will show the near true temperature dependence of the distribution coefficient for the *n*-type dopants considered. Plots of distribution coefficient against temperature are shown in fig. 8. As mentioned previously, a plot of temperature against layer thickness during growth, could be taken as linear over most of the relevant temperature range and hence it was possible to attribute a definite temperature to each level within the grown layer. The distribution coefficient was calculated from $k = C_S/C_L$ making no allowances for possible errors due to evaporation losses. However, these losses were proved negligible for the donor impurities investigated.

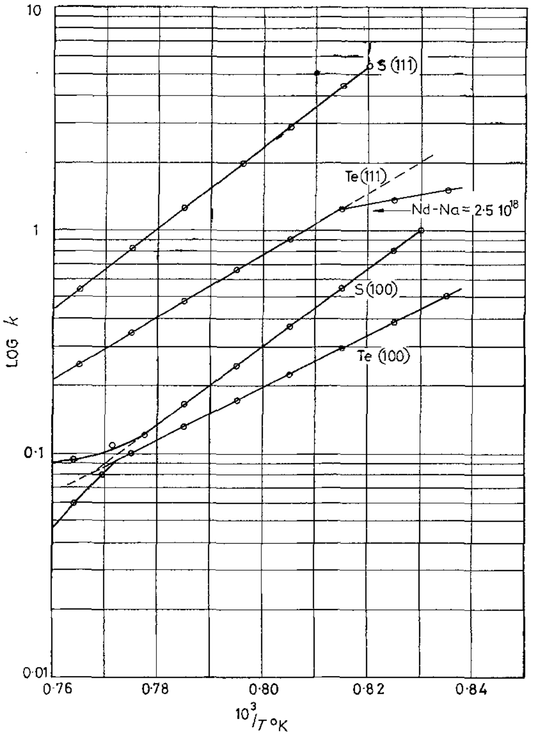

Figure 8 Effective distribution coefficient as a function of temperature for S and Te doped liquid epitaxial layers of GaP grown on (100) and (111) orientated substrates.

The use of electrical measurement techniques rather than the more commonly used chemical tracer method, for the impurity profiling of semiconductors can account for the changes in gradient observed in the plots of distribution coefficient against temperature shown in fig. 8. Hall effect and Schottky barrier methods both measure the net carrier concentration $N_D - N_A$ or vice versa, rather than the true chemical impurity level, and as a result, it has to be assumed that each dopant atom incorporated in the lattice is singly ionised [3]. If the concentration of n-type impurity exceeds 2×10^{18} cm^{-3} precipitates of the dopant can occur in the lattice leading to a lower value of $N_D - N_A$ than expected and for (100) material, $n = 5 \times 10^{16}$ cm^{-3} the background impurity level becomes comparable with the intentional doping, hence the measured $N_D - N_A$ may not be that predicted from the distribution coefficient and the concentration in the liquid melt.

4.2. p-type Material

Our results indicate that the incorporation of zinc in gallium phosphide is an equilibrium process, not kinetically controlled and as such is unaffected by parameters such as cooling rate or stirring. This is in agreement with the observations of Saul and Hackett [18]. As the diffusion rate of zinc in molten gallium at the temperatures concerned is some 10^2 greater than the fastest growth rate this result confirms the proposed mechanism. The temperature dependence of the distribution coefficient for zinc in gallium phosphide deduced from the doping profile is plotted in fig. 9.

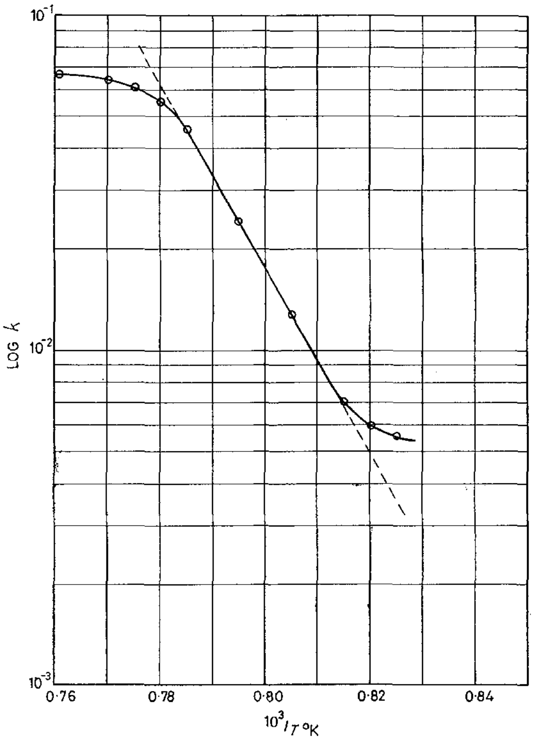

Figure 9 Effective distribution coefficient as a function of temperature for Zn doped liquid epitaxial layers of GaP grown on (111) orientated substrates.

Deviation from the straight line at the high temperature region is probably due to the diffusion of zinc in the solid after growth levelling out the doping gradient. This is a very significant mechanism while the temperature of the melt is of the order of 1000°C, as diffusion across the grown layer-substrate interface is occurring because of the concentration gradient [19]. The deviation of the plot from a straight line for the later stages of growth show the effect of zinc loss due to evaporation, thus depressing the carrier concentration below the expected value.

If evaporation losses were minimised and all the zinc atoms incorporated in the lattice were singly ionised [20] then fig. 9 would represent the temperature dependence of the distribution coefficient for zinc in gallium phosphide.

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References

1. R. H. SAUL, J. ARMSTRONG, and W. H. HACKETT, JUN . *Appl. Phys. Letts.* **15** (1969) 229.
2. R. A. LOGAN, H. G. WHITE, and W. WIEGMANN, *Solid State Electronics* **14** (1971) 55.
3. F. A. TRUMBORE, H. G. WHITE, M. KOWALCHIK, R. A. LOGAN, and C. L. LUKE, *J. Electrochem. Soc.* **112** (1965) 782.
4. A. MOTTRAM, A. R. PEAKER, and P. D. SUDLOW, *ibid* **118** (1971) 318.
5. H. NELSON, *RCA Review*, Dec. (1963).
6. K. K. SHIH, J. M. WOODALL, and L. M. FOSTER, *J. Appl. Phys.* **39** (1968) 2962.
7. M. C. ROWLANDS, "Gallium Arsenide Lasers" (John Wiley, London, 1969) 156.
8. S. J. BASS and P. E. OLIVER, *J. Crystal Growth* **3** (1968) 286.
9. A. R. PEAKER and B. L. SMITH, *Solid State Electron.* **13** (1970) 1407.
10. H. G. B. HICKS and P. D. GREENE, *Int. Symp. GaAs* (1970) 18.
11. M. RUBENSTEIN, *J. Electrochem. Soc.* **112** (1965) 1010.
12. R. N. HALL, *Phys. Rev.* **88** (1952) 139.
13. R. L. LONGINI, A. I. BENNETT, and W. J. SMITH, *J. Appl. Phys.* **31** (1960) 1204.
14. J. A. BURTON, R. C. PRIM, and W. P. SLICHTER, *J. Chem. Phys.* **21** (1953) 1989.
15. J. C. BRICE, "The Growth of Crystals from the Melt" (North Holland, Amsterdam, 1965).
16. A. I. BENNETT and R. L. LONGINI, *Phys. Rev.* **116** (1959) 53.
17. R. H. SAUL and W. H. HACKETT, JUN., *J. Appl. Phys.* **41** (1970) 3554.
18. *Idem*, *J. Electrochem. Soc.* **117** (1970) 921.
19. A. R. PEAKER, P. D. SUDLOW, and A. MOTTRAM, International Conference on Crystal Growth, (Marseille, 1971).
20. L. M. FOSTER, J. F. WOODS, and J. E. LEWIS, *Appl. Phys. Letts.* **14** (1969) 25.

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