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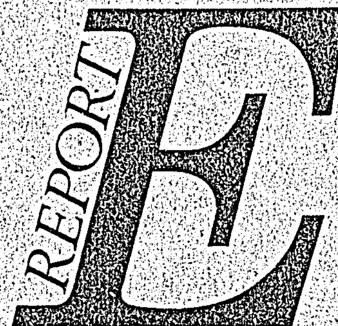
D.ALEXIEV, M.EDMONDSON, K.S.A. BUTCHER & T.TANSLEY

JULY 1992



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ABSTRACT

Liquid phase epitaxy of gallium arsenide has been investigated intensively from the late 1960's to the present and has now a special place in the manufacture of wide band, compound semiconductor radiation detectors. Although this particular process appears to have gained prominence in the last three decades, it is interesting to note that its origins reach back to 1836 when Frankenheim made his first observations.

A brief review is presented from a semiconductor applications point of view on how this subject developed.

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LIQUID PHASE EPITAXIAL GROWTH; GALLIUM ARSENIDE; HISTORIC REVIEW, SOLVENT GROWTH; SILICON INCORPORATION; HYDROGEN ATMOSPHERE; SILICA BOAT

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.

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1. HISTORICAL INTRODUCTION

Liquid phase epitaxy (LPE) is the precipitation from a liquid phase of a crystalline layer onto a parent substrate such that the crystallinity of the substrate is maintained in the grown layer. Such crystal growth has received continuing attention since first observed in natural formations. These observations lead to experimental studies and it appears that Frankenhein (1836) was the first in a long line of crystal growers to grow LPE layers. Frankenhein found that sodium nitrate grew from solution in an oriented direction on the surface of freshly cleaved calcite crystals. Baker (1906) extended this early work with a series of systematic experiments in which a number of related structures were grown upon each other. Baker's method consisted of placing a drop of saturated solution of alkalides onto a cleaved surface and observing the nucleation of crystalline structure through a microscope. Royer (1928) continued Baker's work, and work with the aid of the newly discovered X-ray diffraction analysis of structures, greatly increased the scope of studies of the epitaxial layers. Royer developed rules for epitaxy, of which the most important is that oriented growth occurs only when it involves the parallelism of two lattice planes which have lattice networks of identical or quasi-identical form and closely similar spacings. The term 'percentage misfit' evolved, referring to the differences between the lattice network spacings or "lattice parameters'. Royer found experimentally that lattice-parameter misfit should be no more than 15% as demonstrated by the growth of alkali halides upon other alkali halides and on mica. Electron diffraction studies by Finch and Quarrell (1933) added a further insight into epitaxial growth and misfit. They showed that growth can occur with an initial oriented film which has a modified crystalline structure. The bulk structure of the epitaxy is then constrained so that the lattice plane parallel to the substrate remains identical in size. J.H. van der Merwe (1949) continued with this approach and developed a theoretical approach to epitaxy and the formation of the 'misfit' layer. His theory also predicted a limit, in magnitude, to the misfit of the lattice network beyond which epitaxial growth cannot proceed, similar, as had been found by Royer. Later, in a detailed review D.W. Pashley (1956) concludes that a small misfit is not an essential criterion for epitaxial crystal growth to occur. He find Royer's results very convincing in that the misfit value is significant under certain conditions. However, the theoretical derivation by van der Merwe - the concept of pseudomorphic monolayers - is not correct for many cases of epitaxy. Pashley stresses that chemically grown deposits require special attention since the substrate undergoes changes during the growth of a surface layer; requiring both experimental and theoretical studies of the nucleation problem. It is interesting to note that the special conditions of substrate melt-back and super cooling during the initial epitaxial growth stages have not yet been introduced by experimentalists.

The modest but continuing interest in epitaxy, and in particular liquid phase epitaxy, changed abruptly with the development of the semiconductor industry in the early 1960s. Semiconductor technology at that time was based entirely on germanium with silicon becoming dominant later. However, it was found that Ge and Si had certain limitations for particular device construction. Their band gaps are indirect and are fixed at $E_g(Ge) \simeq 0.68$ eV and $E_g(Si) \simeq 1.1$ eV. Hence, they are not useful as light emitters, transferred electron devices (Gunn oscillators) or efficient solar energy converters (Holonyak et al (1978)). When constructing room temperature operating radiation detectors, high band gaps are required such as $E_g(GaAs) \simeq 1.41$ eV to reduce thermally generated leakage currents and high purity with very low carrier concentration is needed to create large depletion volumes in these devices.

In general, it is these special properties in the III-V semiconductor materials, that led to concentrated research activities from 1966 to the mid-seventies into liquid phase epitaxial layer growth.

2. MODERN APPROACH TO LPE GROWTH OF GALLIUM ARSENIDE

A successful and simple method (Figure 1) for growing LPE GaAs crystals was introducted by H. Nelson (1963). This involved heating a GaAs seed (substrate) next to a solution of tin-GaAs mixture placed at the lower end of a graphite crucible. The graphite crucible is then heated to about 640°C. When the furnace reaches the selected temperature (Figure 2), the power is turned off and the furnace tipped so that the molten tin covers the exposed surface of the GaAs wafer. When cooled to about 400°C, the furnace is tipped back to its original position. Immediately afterwards the graphite crucible is removed and any remaining tin is wiped off the epitaxial layer.

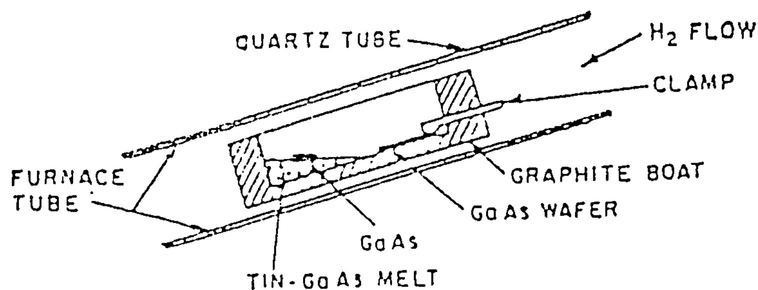


Figure 1 - Apparatus for LPE growth of GaAs from a tin solution (after Nelson, 1963).

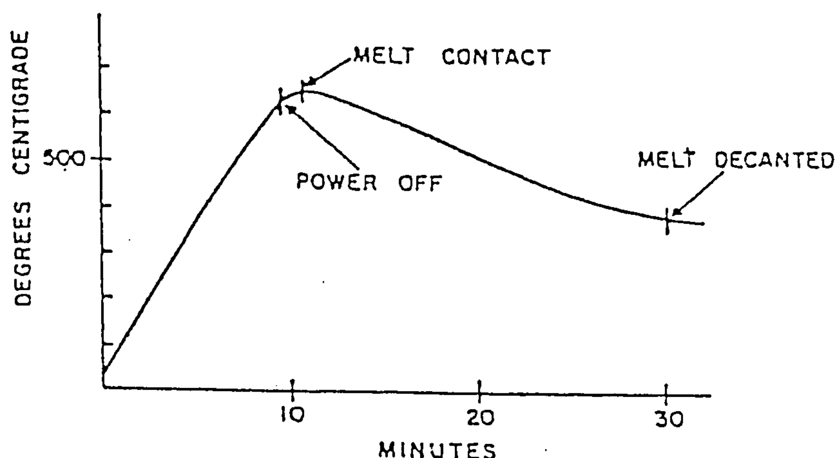


Figure 2 - Heating schedule for expitaxial deposition of GaAs from a tin solution (after Nelson, 1963).

Nelson reported epitaxiel layers that were typically 60 to 80 μm thick. Surfaces were rough due to rapid growth in the low temperature regime near the completion of the process and large (in the order of several μm) droplets of Ga were also noted at the interface. A.R. Goodwin et al (1968) recognised this problem of rapid growth. Their solution was to introduce a temperature gradient, approximately 10°C cm^{-1} so that the seed was always colder than the melt by a fixed amount. As before, the boat was tipped at 850°C and the furnace temperature lowered at a rate of 10°C/min to 600°C. Thus layers of 150 to 200 μm thickness were grown over 3 hours. The surfaces of the epilayer were good and occasionally mirror bright. Such experimental work led Goodwin et al to reconsider the travelling solvent technique (TST) reported earlier by Mlavsky and Weinstein (1963). The Ga solvent is saturated with As by adding GaAs crystals, some are dissolved while others remain floating on the surface throughout the growth cycle. Difficulties were encountered when the melt did not melt the surface of the seed, a problem apparently overcome by preliminary baking of the seed in vacuum at 800°C.

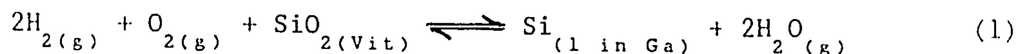
The role of constitutional supercooling in the solution growth of GaAs was first reported by Tiller (1968). He pointed out that if the temperature gradient at the interface is unsufficient, then constitutional supercooling will occur, rendering the interface unstable and resulting in both an uneven surface quality and gallium inclusions. Taller thus derived minimum required values for the temperature gradient in a steady state, diffusion limited growth process. This work was extended by Minden (1969) who derived detailed diffusion equations for the minimum allowable temperatures to avoid constitutional supercooling.

In the same year Hicks and Manley (1969) used Nelson's method to produce LPE GaAs with exceptionally low carrier concentrations in the order of 10^{12} cm^{-3}. A maxmimum mobility of 2.5 x 10^{5} cm^{2}/V-sec at 51K was reported. Two important steps were introduced, firstly the melt was baked at 850°C for 14 hr under a flow of H_2 and secondly, the purity of the feed material was maximised to a net carrier concentration of 10^{15} cm^{-3} and a copper content not greater than 0.1 part per million, the solvent Ga was 99.9999% purity.

Following tipping, the furnace was linearly cooled at 25°C h^{-1}. The substrate used was a semi-insulating Cr-doped single crystal with a <100> orientation. Hicks and Manley noted that some of the LPE layers were highly non-uniform in mobility, suspecting inhomogenity (off-stoichiometry) in the LPE rather than a variation in impurity concentration.

It is interesting to speculate that the non-uniformity of mobility could have been due to substrate melt-back into the Ga solution during tipping, despite the melt being saturated at the growth starting temperature. Freed Cr could then have formed semi-insulating regions in the epitaxial growth front.

In a following publication Hicks and Greene stressed the importance of the quality of the hydrogen atmosphere used during the LPE growth; they produced a theoretical study, with experimental support, of the evolution of free Si (now known to be a shallow acceptor level in LPE GaAs, concentration in the Ga solvent. Hicks and Greene found a direct proportionality between free Si concentration in the Ga solvent and the net hole concentration in the epilayer. They showed that silica boats are reduced by the hydrogen atmosphere, introducing free Si into the Ga solvent as a significant contaminant. When a small controlled quantity of O_2 is introduced into the gas stream, H_2O is produced in the hot furnace so that the free Si contamination in the melt is limited to an acceptable level. The equilibrium concentration of Si in the Ga melt (solvent) is expressed simply as

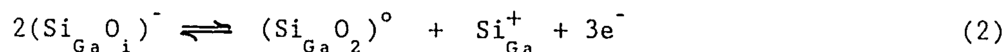


$$2H_{2(g)} + O_{2(g)} + SiO_{2(Vit)} \rightleftharpoons Si_{(l\ in\ Ga)} + 2H_2O_{(g)} \qquad (1)$$

This crucial reaction does not involve As. Ga appears only indirectly as a solvent for the silicon. Hicks and Greene noted that such control of silicon contamination is not only relevant to the growth of LPE of GaAs but is important for the growth of any gallium compound by the same technique. The crucial equation (1) does not contain arsenic and gallium appears only indirectly as a solvlent for the silicon. By applying these principals Hicks and Greene produced epitaxial layers of

remarkably low carrier concentrations in the 10^{13} cm^{-3} range and high electron mobility $\mu^{e}_{77} = 100$ k cm^2 v^{-1} s^{-1}. Eberhardt et al constructed a high resolution X-ray detector from samples of this material. The device was a simple surface-barrier radiation detector in which a measure of the carrier concentration confirmed a value of 2×10^{13} cm^{-3}. However, they also found a typical epitaxial-substrate interface (ESI) layer ranging in thickness up to 2 nm. These ESI layers represent an anomalous discontinuity in the carrier concentration acting as a semi-insulating layer. This ultimately degrades the performance of the device if the substrate is to be used as the ohmic contact. When used as an X-ray spectrometer to resolve ^{241}Am, a resolution of 640 eV FWHM was obtained for the 59.54 keV γ line. The detector was cooled to 122 K to reduce reverse leakage current (I_R) and thereby optise resolution. A ^{57}Co spectrum at room temperature produced 2.6 keV FWHM for the 122 keV γ line. It is interesting to note that the resolution obtained by Eberhardt el al (1971) has not since been bettered in LPE GaAs.

A further insight into the behaviour of Si in GaAs has been gained by M.E. Weiner (1971). A model was proposed based on the formation of silicon-oxygen pairs to explain a variety of anomalous behaviour of LPE GaAs when grown with Si, SiO_2 and O_2. Weiner suggested that Si atoms on Ga sites paired with interstitial oxygen atoms. They form a complex which behaves as an acceptor with energies of 0.1 and 0.4 Ev below the conduction band. The complex is assumed to dissociate upon annealing below 850°C by the reaction:



$$2(Si_{Ga}O_i)^- \rightleftharpoons (Si_{Ga}O_2)^o + Si^+_{Ga} + 3e^- \quad (2)$$

At higher temperatures this reaction may be reversed, thereby explaining changes from n to p type conductivity as a function of Si concentration in GaAs grown from Ga solution in a silicon boat. This model contradicts that of Hicks and Greene, which simply concludes that addition of oxygen slows the reduction process of the silicon boat by the H_2 atmosphere and ultimately lowering the acceptor density in the epilayer.

In a further study of the problem of Si contamination of GaAs, Weiner (1972) proposed three specific cases, of which the first two, shown in Figure 3, are of particular relevance to LPE growth:

Case A: The contamination from an inert crucible or boat in a flow of H_2: here the Si incorporation into the Ga liquid becomes significant only at larger temperatures (> 800°C) and in a very dry H_2 flow over long periods. Weiner's calculations were based on local thermodynamic equilibrium when the initial pressure of water ($P_{H_2O^{\circ}}$) in the system, including any water

from reaction between H_2 and O_2, is increased. He found that the rate of contamination depends only slightly on $P_{H_2O}°$ but when the $P_{H_2O}°$ is increased by the introduction of O_2 then the rate of Si contamination drops rapidly; this is because a significant fraction of total H_2O content is generated by the H_2 reduction of the SiO_2 furnace tube in a very dry system.

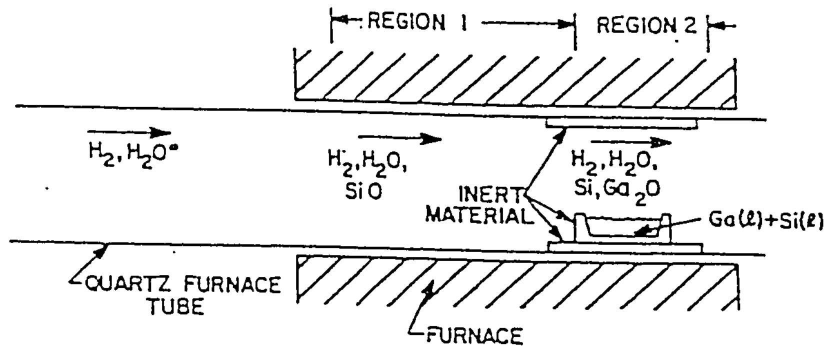


Figure 3 - Case A

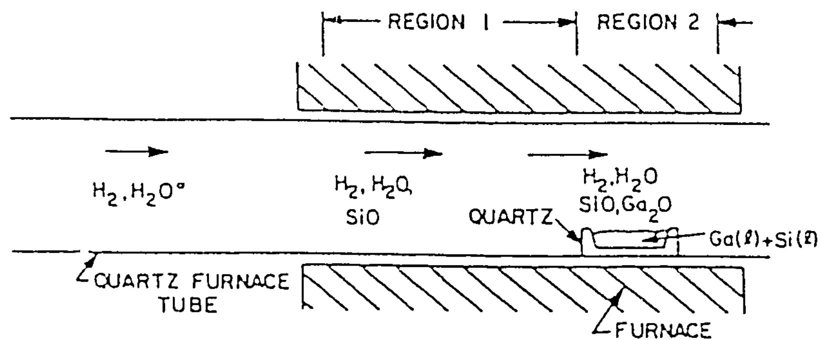


Figure 3 - Case B

Case B: Si contamination when the Ga is located in a quartz crucible (such as used by Hicks and Green and by the author). Most of the Si contamination in the Ga liquid is provided by the Ga reduction of its quartz crucible. The Si contamination rises very rapidly under dry H_2 conditions, such that after 1 hr at 1000°C 10 ppm of Si can be expected in the Ga. However, if more than 10^{-4} atm pressure of water vapour is added to the system, the Si steady-state value is significantly reduced. An interesting observation made by Weiner is that there is a significant decrease in the Si steady-state concentration if the H_2 is replaced with an inert gas. P.B. Greene (1973) considerably simplified Weiner's kinetic and thermodynamic calculations. Essentially Greene used the same approach as earlier (Hicks and Greene) but extended the calculation to the rate at which Si concentration changes in the melt as well as the steady state equilibrium concentration. He showed that, in particular, it is H_2O rather than Ga_2O that is the predominant species involved in O_2 removal from the crucible vicinity (<1000°C). This means that the rate at which reduction occurs and at which Si enters the Ga liquid, is determined by the rate at which H_2O concentration up stream [H_2O input] minus the H_2O downstream and out of the crucible can be removed by the H_2 flow. Green maintains that his earlier, extremely high purity LPE-GaAs ($N_D \simeq 10^{13}$ cm^{-3}), growth results was only possible when water vapour was added to the H_2 stream and when the growth was commenced at a particular temperature. An appreciation of this condition can be seen from the simple differential equation, (adapted from Greene) expressing the rate at which Si enters the Ga liquid.

Rate at which Si enters the melt:

$$\frac{dN_{Si}}{dt} = \frac{([H_2O\ out] - [H_2O\ in])F}{2RT_m}$$

$$= N_{Ga} \frac{d[Si]}{dt}$$

(since in the temperature range of interest the melt consists mostly of Ga),
and on the assumption that H_2O downstream is the equilibrium value for the solution in the crucible:

$$\frac{d[Si]}{dt} = \frac{((K_R^*/[Si])^{1/2} - [H_2O\ in])F}{2RT_m N_{Ga}}$$

when the silicon concentration is very small, the term $[H_2O$ in] is negligible compared with the term $K_R^*/[Si])$ so that the above expression reduces to

$$\frac{d[Si]}{dt} = \frac{K_R^*/[Si]^{1/2} F}{2RT_m N_{Ga}} \qquad \text{(where } F = \text{gas flow and } K_R^* = [Si][H_2O]^2)$$

With the additional condition that [Si] = 0 when t = 0, the solution of the simplified differential equation is

$$[Si] = K_R^{*1/3} (3F/4RT_m N_{Ga})^{2/3} t^{2/3}$$

The important feature of this solution is that it takes longer to reach equilibrium at higher temperatures since the temperature dependence (arising only from the variation of K_R^* with temperature) of the silicon concentration is much less than the temperature dependence of the final (equilibrium) value, which depends on K_R^* to the power of one.

To illustrate this condition, Greene evaluated the differential equation for temperatures of 800°C (Figure 4a) and 1000°C (Figure 4b) at various water concentrations with a flow of 1 litre min^{-1} of H_2 and 25g of gallium melt.

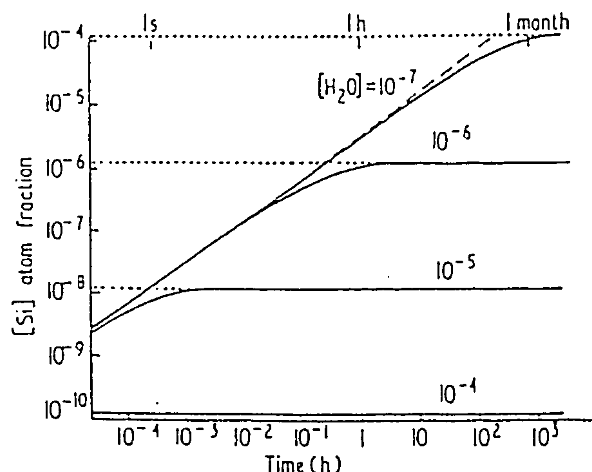


Figure 4a) - Silicon contamination of liquid gallium in a silver boat at 800°C.

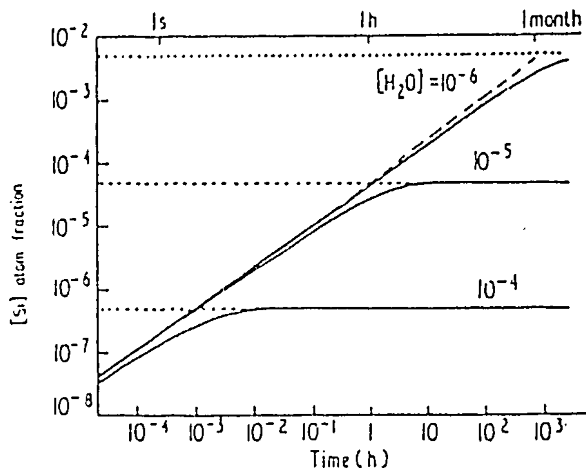


Figure 4b) - Silicon contamination of liquid gallium in a silicon boat at 1000°C (Green, 1973).

The graphs show that high levels of silicon contamination arising from the use of high temperatures and low water concentrations in the gas stream require extremely long times to approach equilibrium. When conditions are chosen to limit the silicon contamination of the melt to less than 1 part in 10^7, the equilibrium concentrations are attained rapidly.

Epilayers between 0.5 to 1 μm thickness are required for construction of devices such as bipolar GaAs transistors, FETs, LEDs and Gunn diodes. The Nelson tilt-tube furnace is not suitable, since the surface morphology, uniformity and thickness are not reproducible. For this reason Vilms and Garrett (1971) introduced a graphite crucible which minimised the retention of Ga droplets, facilitating thickness control by allowing continuous agitation of the Ga solution without sliding seals. Vilms and Garrett's main concern was air leaks into the growth apparatus at seals and at the H_2 purifier membrane. They suggested that oxygen is the impurity responsible for acceptor and donor concentrations in the range 10^{15} to 10^{16} cm^{-3}. At higher temperatures, 700 to 850°C then the donor formation dominates by a factor of 2 to 4. A more quantitative analysis of oxygen induced donors was not made due to difficulties in measuring the low levels of contamination involved. It is important to note at this point that the change from Hicks and Greene's quartz crucible to a graphite reactor introduced a shallow carbon acceptor. The transport of C by evolved oxygen in the form of CO into the epitaxy was not appreciated at that time. Deep Level Transient Spectroscopy (Lang (1974)) analysis would have revealed such a defect in a simple and routine way had it been available. Vilms and Garrett did note an acceptor impurity, the concentration of which varied

with temperature, its identity was not established. Vilms and Garrett reported an activation energy of 1.52 eV, consistent with either vacancy formation or substitutional impurity incorporation. They speculated that the acceptor is either a native defect formed during the epitaxial growth, or that there is residual impurity with a large segregation coefficient in the solution and a consequent strong dependency on growth temperature.

Since Vilms and Garrett's main intention was to grow epitaxial layers in the 0.5 to 20 μm thickness range, particular care had to be placed onto uniform nucleation of the epilayer and onto the removal of the structure from the solution at termination of growth. Surfaces were cleaned, lapped and chemically-mechanically polished with a bromine-methanol etchant on an inert polishing pad. Finally, the samples were given a light etch in H_2SO_4 : H_2O_2 : H_2O = 3:1:1, currently a standard etchant for GaAs.

Graphite related growth arrangements were followed by the invention of the sliding-boat technique by Hayashi et al (1969) and Blum and Shih (1971). Here, the substrate is positioned in a machined graphite holder that can slide to contact in sequence several wells containing the saturated Ga solution. This method can give rise to a form of "volume-limited" growth, because the wells contain only a very small amount of the solution and spontaneous nucleation is thereby avoided.

Most LPE growth techniques involve some predetermined rate of cooling of a saturated gallium melt. In general these techniques are suitable for thin layers (~ 100 μm) but fail for thicknesses of more than a few hundred microns. The inherent reason is that the temperature interval used dictates the thickness limit. Disadvantages are also found in the doping profiles which vary as the growth proceeds as a consequence of temperature dependent segregation coefficients. For such reasons attention has been directed to the travelling solvent growth techniques first developed by Mlavsky and Weinstein (1963). A modified version of this technique was introduced by Hesse et al (1972). Simply put, a temperature gradient about a constant mean temperature transports the dissociated As from the GaAs feed material to a substrate via a gallium solvent.

In this case the temperature profile is maintained by the axial temperature distribution of the furnace and the location of the crucible. The placement of the feed material in relation to the substrate now clearly becomes a critical parameter. In general, LPE layers produced by such arrangements have shown poor crystallinity, suggesting that constitutional supercooling occurs due to insufficient temperature gradient. However, layer thickness exceeding 600 μm were

achieved over a four hour period. Radiation detector diodes constructed in the form of a series of 'dots', were found to vary in both resolution and leakage currents suggesting to Hesse et al considerable lateral inhomogeniety in the epitaxial layer.

The nature of the previously mentioned anomalous layer also known as the i-layer has been of continuing interest, it is a high resistance epitaxy to substrate interface layer found in LPE and vapour phase epitaxy (VPE). This layer tends to be in the region of 0.2 to 2 μm wide and, because it includes a significant dip in the net carrier concentration profile, exhibits capacitive attenuation when fabricated into a device. This detrimental effect of the anomalous interface is well known in the construction of surface barrier radiation detectors and Gunn oscillators.

Blocker et al (1970) produced a detailed study of the interface layer by scanning electron microscopy and a series of capacitance-voltage (CV) measurements. They found that this region has a typical net acceptor density ranging from 10^{14} to 10^{16} cm^{-3} which can be explained simply as an alteration in the balance of the net carrier concentration across a step transition from n^{+} to n^{-}. Since the substrate is nearly compensated so that N_D and N_A are both very much greater than $/N_D - N_A/$then an amphoteric impurity such as Si can alter this balance towards an acceptor state under a strain or temperature gradient. Similarly, "natural" impurities such as C could become electrically active by changing their lattice position. Alternatively, surface preparation of the substrate could leave a p-type impurity (e.g. Cu) at the liquid-solid interface growth front. Support for the last possibility came from photoluminescence studies of the interface layer by Nakashima and Hiras (1970) who found an emission band due to Cu acceptors at the interface layer. Further insight was gained by Di Lorenzo et al (1971) using direct image mass analysers and finding that these regions contain high concentrations of localised Si impurities with lesser concentrations of Li, Al and Fe. Further substance to this claim was given by Gibbons et al (1972) who suggested that poor device (diode) characteristics were due to an abrupt change in the free carrier concentration related to an impurity gradient between the epitaxial layer and the substrate. They considered that a desirable solution would be to introduce a buffer layer about 20 μm thick between the substrate and epilayer. However, growing such a configuration with a buffer concentration of 10^{15} cm^{-3} proved difficult with only one growth producing good devices. An expected improvement in the I-V characteristic was not found. The anomalous layer was further investigated by Tavendale et al (1972). They found that when a radiation detector (essentially a diode under reverse bias) was exposed to infrared illumination a marked improvement was noted in the stability of pulse height response with bias and multi-peaking resulting from

capacitative attenuation near full depletion of the diode. This effect can be explained simply as an increase of the conductivity of the anomalous layer as deep level acceptor impurities located there are field-deionised. The detector then tends towards real operation. The deionising of the anomalous layer acceptor does not exclude the possibility that other deep level defects are present in the bulk of the epitaxy. These might include deep donors which are deionised and similarly reduce pulse height variation. A further comment by Tavendale et al on reducing the effect of the anomalous layer is by using much deeper depletion layer. The capacitance radio aspect of the two layer would then give a lower charge attenuation. This would require high purity and LPE layers in excess of 200 μm thickness.

A different method from transient systems based on Nelson dip growth is the steady-state growth developed by Long, Ballantyne and Eastman (1974). This method allows lower growth temperatures and arbitrarily thick layers. Growth is achieved by establishing an equilibrium at the growing interface with a fixed temperature gradient between the substrate and a source crystal of undoped GaAs. The driving force for transporting As across the solution to the substrate is the temperature gradient. Transport is either by diffusion or by a combination of diffusion and convection which may account for the poor thickness uniformity commonly found. However, the advantage of thicker layers was outweighed by poorer purity in the 1 to 2.5 x 10^{15} cm^{-3} range and surface variations dominated by edge effects. The vertical growth geometry, Figure 5a) and 5b) has the crucible and the seed, saturated Ga and the GaAs source are located at appropriate points in the vertical temperature profile.

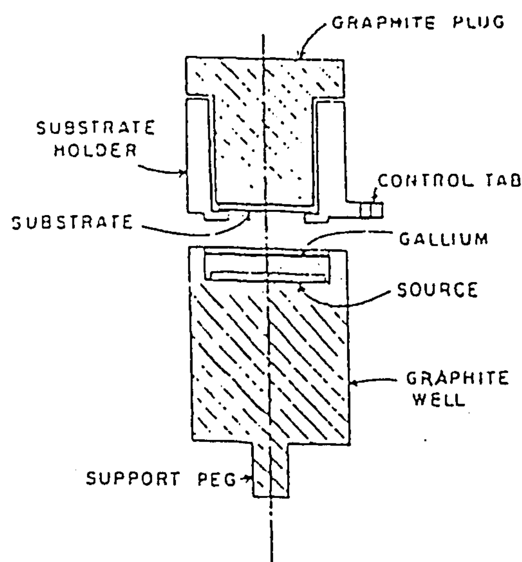


Figure 5a) - Vertical steady-state boat in which the substrate is on top of the solution (after Long et al, 1974).

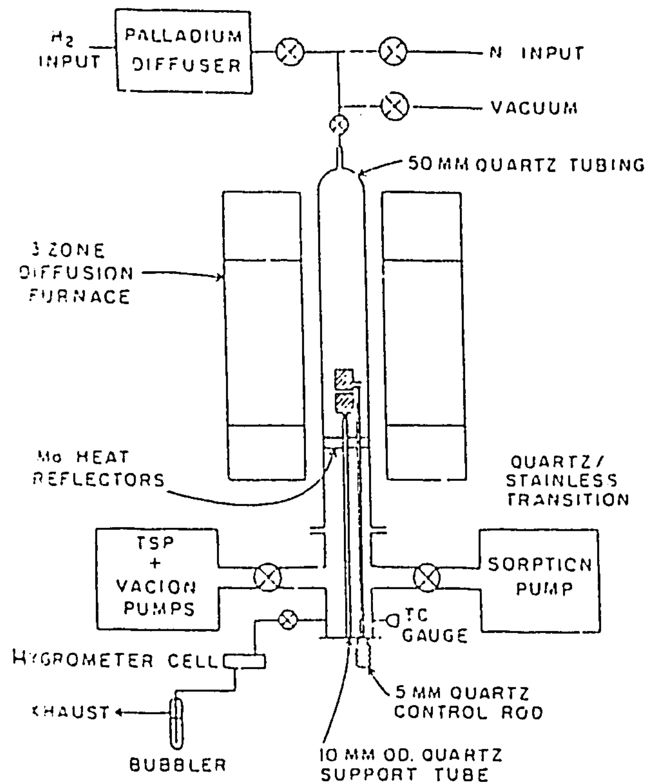


Figure 5b) - Vertical steady-state growth system (after Long et al, 1974)

Similar vertical growth arrangements were implemented by others, in particular Kobayshi et al (1976) used a simple dipping-type procedure. They eliminated poor control during the growth and especially over termination where Ga droplets often remain on the newly grown epilayer and result in uneven surfaces. The growth system consists of a graphite boat and the high quality palladium purified H_2. The resulting epilayers were of good quality with carrier concentration in the range of 10^{12} to 10^{14} cm^{-3}. Charge trapping was noted and attributed to a deep acceptor produced by assumed Si contaminants, to reduce this adverse effect Fe was added (one part in three hundred) to the Ga melt. Excellent spectral results were obtained from surface barrier detectors built from such material.

Despite these numerous variations in LPE growth systems, defects and poor surface morphology resulting from uncontrolled microscopic growth velocity remained a problem. Joffe (1956) and Pfann et al (1957) suggested novel method to influence and control growth of an epitaxy in the immediate vicinity of the interface. The arrangement is a typical vertical growth configuration modified to permit passage of an electric current. In such a way Peltier cooling (or heating) is introduced at the substrate-liquid interface. Kumagawa et al (1973) sucessfully used such a method, known as liquid-phase electroepitaxy (LPEE).

This earlier work was further developed by Jastrzebski et al (1978), (1980) and (1986) who produced a number of publications on growth kinetics in LPEE. Their method achieved bulk crystal growth up to 4mm thickness over a 20mm diameter wafer. The structure was of high quality, being essentially dislocation free. The net carrier concentration for such material could not be reduced below 10^{15} cm^{-3} suggesting that passage of an electric current adversely affects impurity segregation in the growth front of the epitaxy. Further work on purification of LPEE layer by Bryskiewicz et al (1978) produced lower carrier concentrations in the order of 10^{14} cm^{-3}. Photoluminescence (PL) was used to identify the Si acceptor as the dominant residual impurity. This was uniformly distributed through the LPEE, again confirming that segregation can be adversely affected by the electric current through the melt.

3. RECENT ADVANCES IN GaAs MATERIAL

In this section, advances in GaAs material growth, characterisation and device fabrication within the previous five to six years, are reviewed. These advances reflect the considerable R&D effort now being applied to GaAs, especially for optoelectronic, microwave and fast-logic devices.

To accommodate large volume production from single wafer GaAs, some significant improvements have been made in the growth of high resistivity "semi-insulating" ($\rho \approx 10^8 \Omega$-cm) undoped material using the liquid encapsulation Czochralski (LEC) pulling technique. Sumitomo Electric (Japan) have been able to produce commercially very low dislocation (~ 1000 cm^{-2}) material, up to 3 inch diameter, which is ideal for epitaxial substrates. Reduction of Si contamination is also achieved by using pyrolytic boron nitride (PBN) crucibles as reported by Shimada et al (1984).

Continued improvements in the purity of epitaxial GaAs grown by means other than LPE, such as molecular beam epitaxy (MBE) have been reported. MBE layers have been grown undoped at a carrier concentration of 2×10^{14} cm^{-3}, by Hwang et al (1983) but unfortunately, MBE growth is intrinsically slow (~ 1 μm/h) and therefore applicable only to thin layer growth. Andrews (1983) and Abrokwah (1983) have used vapour phase epitaxy (VPE) and produced very low carrier concentrations (10^{12} - 10^{13} cm^{-3}) but again such growth techniques only produce good quantity material at low growth rates of about 1 μm/h. Recent work by Boucher et al (1987) into newly developed LPE electroepitaxy (LPEE) have reported, by way of contrast, the possibility of growing quality "bulk epitaxial crystals" up to 4mm thick with low dislocation densities but relatively poor carrier concentrations, mostly around 1×10^{15} cm^{-3} with a best figure of 2×10^{14} cm^{-3}.

GaAs has electrical properties which are strongly dependent on variations in stoichiometry which in turn depend on growth mode. For example, the dominant deep level defect, labelled EL2, is a deep donor having an activation energy of 0.82 eV to the conduction band. This defect performs a crucial role in the compensation of shallow acceptors due to carbon incorporated during the production of 'undoped' semi-insulating GaAs substrates. These are now used by the electronics industry as an alternative to Cr-doped semi insulating material.

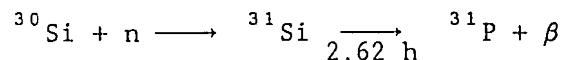
Unfortunately, deep levels remove minority carriers either by trapping or by enhancement of recombination rates, so that the EL2 defect has a deleterious effect on the performance of GaAs devices, particularly nuclear radiation detectors. The EL2 defect has therefore been the subject of intensive investigation and considerable controversy. An understanding of its structure is central to the development of ultra high speed GaAs circuits.

The EL2 defect was originally thought to be oxygen-related (Lagowski et al (1984)) but electron paramagnetic resonance (EPR) studies have indicated that although the defect is present in bulk and VPE GaAs grown under As-rich conditions, it is absent in Ga-rich LPE, material. The defect can be detected by optical absorption or DLTS techniques, reported by von Bardeleben et al (1986) and by Alexiev and Tavendale (1984). Optical methods have been used by Holmes et al (1983) to map EL2 contours in LEC GaAs and show that EL2 formation is also enhanced by crystal stress (reflected by dislocation density). In a recent detailed investigation von Bardeleben et al (1986) attempted to identify EL2 using EPR and DLTS, proposing that the defect is the complex of the antisite defect As_{Ga} and an instrinsic interstitial defect As_i, with As_i in the first or second-nearest neighbour sites relative to As_{Ga} corresponding to the metastable and stable EL2 forms respectively. This description of the EL2 defect satisfied important observations made by Levinson (1983) of charge-state-controlled structural relaxation of the centre and intercentre optical transitions.

There has been considerable interest in the nature of irradiation-induced defects in GaAs, particularly as an aid in determining the structure of, for example, the EL2 defect (Pons and Bourgoin (1985), Stievenard and Bourgoin (1986). Further, the role of thermally induced defects, again involving the dominant EL2 deep donor defect, has recently been demonstrated by Lagowski et al (1986) in so-called inverted thermal conversion (ITC) material. Here, LEC GaAs (conducting or semi-insulating) is first subjected to a high temperature (1100-1200°C) anneal and fast cooling (quenching), which leads to a considerable reduction in the concentration of the EL2 defect, typically to less than 10^{15} cm^{-3}). A second anneal at 800°C (30 minutes) restores the EL2 defect and associated compensation giving high

resistivity ($2 \times 10^{8} \Omega$-cm) n-type material. Kobayski et al (1976) had shown much earlier that it is possible to cycle reversibly between semiconducting and semi-insulating GaAs using LEC grown material having low C and Si concentrationsby either slow-cooling or quenching from 950°C. This effect also involves the EL2 defect compensation of residual acceptors. It is worth noting that these observations present the possibility of thermally controlling the conductivity of GaAs for radiation detector applications but it must also be kept in mind that the presence of a significant concentration of EL2 (or any other trap or records centre) will inevitably lead to poor detector performance, seen usually as asymmetric spectral lines with poor resolution. It appears that the most likely application for ITC - GaAs will be as substrate material.

Neutron transmutation doping of GaAs offers an alternate route for compensation of conducting material. The technique was first demonstrated for Si by Cleland et al (1950) and is now well established in the silicon industry for production of uniformly phosphorus-doped material from float-zone single crystals via the reaction:



$$^{30}Si + n \longrightarrow {}^{31}Si \xrightarrow[2.62\ h]{} {}^{31}P + \beta$$

In the case of GaAs, due to the multiplicity of the natural isotopes of Ga and As the situation is more complex but essentially Ga and As transmute to Ge and Se donors which are electrically activated by thermal annealing. The radioactive β decay period remains reasonably short.

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

It is surprising that the technique was not applied to GaAs until 1970 (Marianashvii and Nanobashvili) to be followed later in a detailed report by Vesaghi (1982). Recently, studies of NTD treated semi-insulating Czochralski-grown GaAs have been reported by Mueller et al (1980) and Kolin et al (1984), NTD doped bulk-grown by Vigdorovich et al (1981) and Alexiev (1987). It appears that in thermal-neutron transmuted GaAs, radiation damage annealing commences at about 500°C and

is completed at about 800°C (Mueller et al (1980) and Yahagi et al (1984)). The anti-site As_{Ga} defect is primarily involved in the annealing process (Schneider and Kaufmann (1982)). The fact that target doping can be attained at reasonably low temperatures for GaAs is encouraging, given the decomposition associated with high temperature treatment of the material.

As in the case of NTD-Si, it should be possible to at least increase the compensation in GaAs by a factor of 10, providing the inhomogeneity in the initial doping is no greater than about 10%. Thus, there is some prospect of reducing the lowest bulk-doped (p-type) GaAs presently available from $N_A \sim 10^{15}$ cm^{-3} to $N_A \sim 10^{14}$ cm^{-3} by the NTD technique. However, this doping level would still be too high for detector applications, and therefore low-doped LPE GaAs as the starting material, preferably with a $N_A \sim 10^{13}$ to 10^{14} cm^{-3} range and p-type, becomes very attractive.

Passivation of both deep and shallow electrically-active defects by hydrogenation of GaAs has recently been the subject of intensive research. The discovery that a number of common deep levels in bulk, polycrystalline or LPE GaAs could be passivated following plasma - hydrogenation was first reported by Pearton (1982), Pearton and Tavendale (1982 and 1983). The EL2 level is also found to be deactivated on hydrogenation (Lagowski et al (1982)) with the electrical activity being restored by annealing at ~ 400°C. In lightly-doped n-type GaAs grown by MBE both shallow donors (e.g. Si) and the dominant deep level centres are neutralised by hydro-genation at 250°C with reactivation of the Si donors on annealing at 400°C and the deep levels at 600°C. Thus there is a temperature window within which it is possible to regenerate doping by shallow centres (controlling carrier concentration) yet still suppressing the deep level trapping centres (Dautremont-Smith et al (1986)). It is also interesting to note that the near-surface free hole concentration in p-type (Zn-doped) GaAs can be suppressed by hydrogenation, indicating neutralisation of acceptors (Johnson et al (1986)). Jalil et al (1987) and Pajot et al (1987) used infrared spectroscopy coupled with isotopic substitution (H substituted with D), and deduced that, in the cases of either, donor or acceptor neutralisation, the hydrogen is bonded to the As atom nearest to the dopant atom (Si or Zn) site.

The use of hydrogenation to passivate or neutralise remanant deep level defects in high purity LPE GaAs, while appearing to be a simple means of upgrading material quality, has the drawback that at most the process is only effective to a depth of a few μm, being regulated by diffusion rates. However, for applications such as passivation of surface-related defects, hydrogenation could well be useful in device fabrication.

In connection with the development of new GaAs device fabrication techniques, a considerable effort has been applied recently to the application of ion implantation doping, particularly for the construction of small dimensional channel or contact regions needed for high speed devices. This has in turn led to the application of new methods of dopant activation, e.g. rapid thermal annealing (RTA) and studies of the residual defects and solubility and activity of the implanted dopants. These topics have been extensively revised by Pearton et al (1987) and Williams and Pearton (1985). It is obvious that these techniques are also applicable to the fabrication of much larger devices such as formation of robust contacts on radiation detectors.

4. REFERENCES

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5. ACKNOWLEDGEMENT

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