Close-Spaced Epitaxial Growth of $GaAs_x P_{1-x}$ from Powder GaAs and GaP

In this note the growth of homogeneous solid solution of $GaAs_xP_{1-x}$ using powder GaAs and GaP by close-spaced epitaxy with water vapour as transporting agent is described. The apparatus used is shown schematically in fig. 1 and is basically the same as that of Nicoll [1]. It consists of two graphite blocks each of which is heated externally by an 800 watt Quartz Iodine lamp (Atlas) housed in reflecting hemispheres specially designed to focus the reflected energies on to the graphite block. The voltages of each lamp are individually controlled, and the reflectors are cooled by a jet of compressed air. The temperature of each graphite block is determined by quartz-sheathed thermocouples embedded in the graphite blocks. The temperature of the upper graphite block in contact with GaAs substrate is maintained 10 to 50° C below the temperature of the source material pressed in the lower graphite block. A spacing of 0.032 in. (1.0 in. = 2.5 cm) was ensured between source and substrate by inserting quartz strips. The hydrogen from a "pure" H_2 cylinder was further purified by use of a JM palladium purifier. The required amount of water was admitted by passing the palladium-diffused hydrogen over crushed ice, maintained by a salt ice bath to a sub-zero temperature. The gas flow rate was of the order of 7 to 10 cm^3, and was difficult to monitor with the flow-meter.

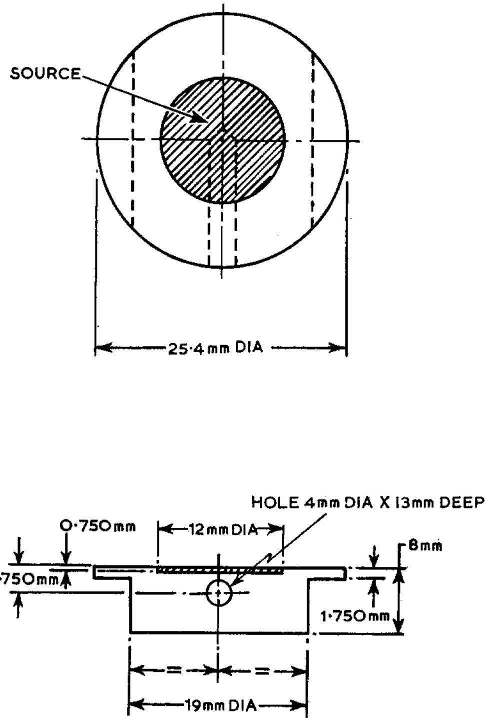


Figure 2 Graphite block with cavity for holding source material.

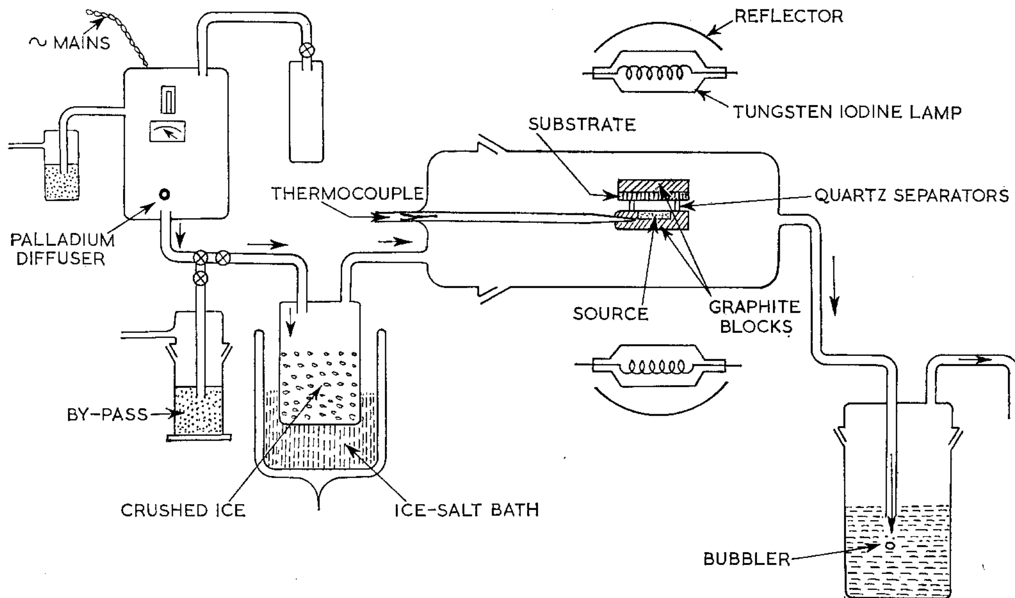


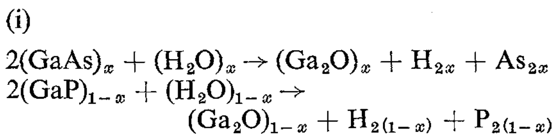
Figure 1 Close-spaced epitaxial system.

GaAs wafers were used as substrate material for preparing $GaAs_xP_{1-x}$ epitaxial layers. It is very important to have a good surface on the substrate for the satisfactory growth of the epitaxial layer. The chemical etchant used for most of the GaAs (100) substrate wafers was 3:1:1 H_2SO_4:H_2O_2:H_2O.

The GaP used in combination with GaAs was prepared in open tube transport by reacting Ga_2O_3 with PCl_3. This GaP was then crushed in an Agate pestle and mortar, sieved through 100 mesh, and treated with hydrochloric acid (HCl) as suggested by Rubenstein [2]. The GaAs was also powdered by pestle and mortar, and sieved, but no acid treatment was given to the GaAs powder. The dried GaAs and GaP powders were mixed together thoroughly, and pressed into the cavity in a graphite block, as shown in fig. 2.

The transport of GaAs and GaP in the presence of water vapour proceeds via the following reaction

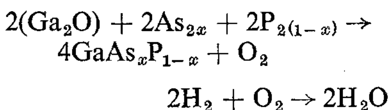
(i)



$$2(GaAs)_x + (H_2O)_x \rightarrow (Ga_2O)_x + H_{2x} + As_{2x}$$

$$2(GaP)_{1-x} + (H_2O)_{1-x} \rightarrow (Ga_2O)_{1-x} + H_{2(1-x)} + P_{2(1-x)}$$

(ii) At a lower temperature



$$2(Ga_2O) + 2As_{2x} + 2P_{2(1-x)} \rightarrow 4GaAs_xP_{1-x} + O_2$$

$$2H_2 + O_2 \rightarrow 2H_2O$$

where x can be varied from 0 to 1.

Ga_2O is the transporting agent as observed by Antkiv and Dibeler [3]. Frosch and Thurmond [4] have also reported that Ga_2O is the volatile species and hence the transporting agent. The geometry of the apparatus demands that all the reactants remain essentially in the region between the two graphite blocks, the rest of the tube remains at ambient temperature.

The source temperature was kept at 950° C and the substrate at 930° C to ensure maximum efficiency in the transport mechanism as obtained by Koike [5] and confirmed by Gottleib [6] who demonstrated that when there is a small temperature difference between source and substrate the surface is mirror-like, while 50° C temperature difference between source and substrate produces mostly rough surface of the grown material. The substrate GaAs wafers were all of n-type, with carrier concentration of 10^{17} to 10^{18} carriers/cm^3. No experiment was performed with semi-insulating GaAs substrate, due to difficulties encountered in earlier experiments on the growth of pure GaP on semi-insulating GaAs substrate in the close-spaced epitaxial process [7]. The growth of material as obtained is given in table 1. In samples 1 and 14, $GaAs_xP_{1-x}$ synthesized compound was used in powder form, pressed into the cavity of graphite block. This type of compound powder always gives single-phase, single crystals of the above material. In case of mixed powder, the epitaxial layer was either single-crystal or polycrystalline material. However, if the second run is made with the same source in the cavity, better results are obtained as can be seen from samples 3, 6, 9, and 10. It seems that in the first run, materials get synthesised and form a pallet. Once a pallet has been formed it gives single-phase single crystals in most of the cases.

The grown layer represents the mixture of the source composition with slight variation only. The composition of the epitaxial layer was determined by reflectivity measurements as reported by Williams and Jones [8]. The starting material is in the mole ratio of GaAs and GaP powders. It seems from the table, that the epitaxial layer is always rich in GaAs at the cost of GaP. In the case of samples 1 and 14 it was not possible to determine the exact composition of source material, as the original piece of $GaAs_xP_{1-x}$ was a polycrystalline material, with x varying by 0.1 to 0.9 from one end to the other end of the ingot, as well as being non-uniform in the perpendicular direction of the boat length. However, final composition of the epitaxial layer is given in the table. Gottlieb [6] got the composition of the epitaxial layer with only 2% variation from the source material, and therefore we can assume that the composition of the epitaxial layer in samples 1 and 14 is the same as that of the overall composition of source material. For the fabrication of the diode, it was necessary to have Te doping in the GaAs P epitaxial layer. Although no extra Te was added in the powder as such, some of the GaAs powder had Te as dopant, and it seems that Te is also transported to the epitaxial layer corresponding to the amount present in the source GaAs powder.

The author is grateful to Mr P. Gurnell of the Services Electronics Research Laboratory, Baldock, Herts, UK, for facilities provided, and to Dr N. B. Bhatt of this laboratory for arranging the author's deputation to Services Electronics Research Laboratory, where this work was done.

TABLE I

Sr. no.	Composition used GaAs (mol %)	Composition used GaP (mol %)	Composition obtained after growth GaAs (mol %)	Composition obtained after growth GaP (mol %)	Mode of preparing source	Doping if any	Result
1	—	—	83	17	$GaAs_x P_{1-x}$ powdered and pressed in graphite block	Nil	Single crystalline layer
2	50	50	53	47	Powdered GaAs and GaP mixed and pressed in graphite block	Te present in GaAs source	Single crystalline layer
3	50	50	45	55	Remainder of no. 2	,,	,,
4	0	100	0	100	Powdered GaP pressed in graphite block	Nil	,,
5	30	70	35	65	Powdered GaAs and GaP mixed and pressed in graphite block	Te present in GaAs source	,,
6	30	70	35	65	Remainder of no. 5	,,	,,
7	50	50	54	46	Powdered GaAs and GaP mixed and pressed in graphite block	,,	Matt structure
8	50	50	45	55	,,	Nil	Needle growth
9	50	50	52	48	Remainder of no. 8	Nil	Single-crystal
10	50	50	50	50	Remainder of no. 9	Nil	Single-crystal
11	70	30	—	—	Powdered GaAs and GaP mixed and pressed in graphite block	Te present in GaAs source	Polycrystalline
12	90	10	—	—	Powdered GaAs and GaP mixed and pressed in graphite block	,,	Partly single-crystal
13	100	0	100	0	Powdered GaAs pressed in graphite	,,	Single crystalline layer
14	—	—	42	58	Powder pressed of $GaAs_x$ P_{1-x}	,,	,,

References

1. F. H. NICOLL, *J. Electrochem. Soc.* **110** (1963) 1165.
2. M. RUBENSTEIN, *ibid* **112** (1965) 426.
3. S. ANTKIV and V. H. DIBELER, *J. Chem. Phys.* **31** (1953) 1890.
4. C. J. FROSCH and C. D. THURMOND, *J. Phys. Chem.* **66** (1962) 877.
5. T. KOIKE, Standford Laboratory Research Review No. 8 (1964).
6. G. E. GOTTLIEB, *J. Electrochem. Soc.* **112** (1965) 192.
7. R. K. PUROHIT, unpublished work at SERL.
8. E. W. WILLIAMS and C. E. JONES, *Solid State Commun.* 3 (1965) 195.

6 December 1967

R. K. PUROHIT
Solidstate Physics Laboratory
Lucknow Road
Delhi-7, India

The Effect of Chromic Acid on Polypropylene

Polypropylene is an important plastic because of its good combination of strength and rigidity over a relatively wide temperature range. It has been predicted [1] that it will eventually overtake high density polyethylene to become the second largest tonnage polyolefin. Successful use of this material requires data on the influence of cooling rate from the melt on the microstructure, and on the way in which the microstructure deforms under stress. Few data are available however because previously the only ways of revealing the microstructures of bulk test specimens were either by fracturing and examining fracture surfaces or by microtome sectioning. Research at Leeds has shown that the microstructures of bulk polypropylene specimens can be revealed non-destructively using a chromic