Appendix 2

Materials for which environmental superplasticity has been reported.

Material	Test Conditions		Transformation	Maximum elongation per cycle	References
	Stress g mm^{-2}	Temperature range °C			
Fe	550	910	$\alpha - \gamma$	1.6×10^{-2}	92
	800	870–930	$\alpha - \gamma$	1.5×10^{-2}	95
Fe–0.2 wt% C	1600	740–800	$\alpha - \gamma$	2.0×10^{-2}	95
Fe–0.4 wt% C	1800	540–816	$\alpha - \gamma$	4.0×10^{-3}	90
Fe–0.98 wt% C	1800	540–816	$\alpha - \gamma$	4.9×10^{-3}	90
Fe–1.07 wt% C Fe–0.008 wt% N	1800	540–816	$\alpha - \gamma$	$3.3. \times 10^{-3}$	90
Co (spec. pure)	6500	417	$\epsilon - \alpha$	2.0×10^{-3}	92
Zr (iodide)	150	863	$\alpha - \beta$	1.9×10^{-2}	92
Ti (commercial)	180	882	$\alpha - \beta$	3.0×10^{-2}	92
U (commercial)	400	663	$\alpha - \beta$	1.0×10^{-2}	92
	125	770	$\beta - \gamma$	1.3×10^{-2}	92

Letter

Synthesis and Growth of Single Crystals of Gallium Nitride

Transparent single crystals of gallium nitride have been prepared in sizes ranging up to 1 mm thick and 5 mm in length. The growth occurs from a specially treated gallium nitride powder at temperatures of 1150 to 1200°C in a stream of dry NH_3 gas. Hot probe measurements indicate that the crystals are *N*-type and of very high conductivity. The growth takes place most likely by a sintering or surface diffusion process.

There is considerable interest in gallium nitride as a semiconducting compound because of its high bandgap, ~3.25 eV [1]. Light emission from gallium nitride devices can be in the visible or ultraviolet range of the spectrum. Gallium nitride has been made both *N*- and *P*-type [2, 3] and has a melting point estimated to be near 2000°C [4]. Most of the chemical, electrical and optical properties of gallium nitride have been obtained by the study of powdered or microcrystalline material. The method first described by Johnson *et al* [5], in which pure gallium is reacted with ammonia gas at 1000 to 1100°C has been used by most investigators to synthesise gallium nitride. The most comprehensive description of single crystal growth of gallium nitride is given by Rabenau [6]. The largest single crystals described in the early literature appear to be ~5 mm and 10 to 30 μm in diameter [7]. Two recent publications deal with epitaxial deposition of gallium nitride on single crystal substrates. The work of Maruska and Tietjen [2] describes the growth of colourless single crystal gallium nitride on sapphire substrates while Faulkner *et al* [8] report on the deposition of polycrystalline gallium nitride films on silicon carbide substrates. The present paper describes the preparation of colourless hexagonal single crystal needles of gallium nitride from a specially prepared powder. Raman scattering and infra-red absorption measurements have been made on these crystals and will be described in detail elsewhere [9]. The technique used for the synthesis of gallium nitride is an adaptation of the method of Johnson *et al* and is described below.

In a typical synthesis run, 5 to 6 g of 6-9's pure gallium are added to a clean BN boat.* The boat is then inserted into a BN* furnace liner and slowly heated in a stream of tank ammonia to ~1050°C. Gas flow rates are from 30 to 100 cc/min. The reaction begins at 1050°C and is allowed to continue overnight during which time the tube becomes partially blocked with

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*Pyrolytic BN from Union Carbide Corporation.

material. The tube and contents are then cooled to room temperature and removed from the furnace. The reaction products, which include various shades of white, grey and black material along with some unreacted gallium, are then boiled in hot aqua regia to remove all the unreacted gallium and also to dissolve any residual impurity metals that form soluble chlorides. Next, the solution is cooled, filtered, the gallium nitride powder washed with deionised water and methanol, and then dried overnight at 100°C. The dried mixture is then ground to a fine powder and reheated in a BN boat and tube to ~1100°C using 100% NH_3 for ~24 h before use as starting material for single crystal growth. The resulting powder is grey-white in colour. Contrary to some reports in the literature, very little material was observed to vaporise at 1100°C in ammonia gas [6].

The growth of single crystals of gallium nitride was achieved by heating the grey-white powder above 1100°C in flowing ammonia. Boron nitride boats and furnace liners were used to contain the materials. Very little growth of GaN was seen until 1150 to 1180°C was reached. In this temperature range, gallium nitride needles with hexagonal symmetry were grown in a 72 h period, using ammonia flows of ~50 cc/min. Fig. 1 shows a photograph of some clear single crystals grown in this manner. The largest needle is ~5 mm long and ~1 mm thick. The three clusters shown to the left of the photograph were grown during a 72 h period while the two right-hand clusters of gallium nitride grew in a 24 h period. The mechanism by which growth occurs is not known but most probably, surface diffusion phenomena are involved. To date no evidence has been observed of a V-L-S mechanism of growth. When the gallium nitride powder is heated to 1200°C for 24 to 48 h there is evidence of decomposition and some black hexagonal needles have been obtained at this temperature. The darkening of the gallium nitride is probably due to nitrogen vacancies [6]. Growth parameters have not been studied in enough detail to determine the conditions for growth of larger crystals than those so far obtained. However, by following the above described methods, colourless single crystals of variable sizes are always obtained. The clear needles show high conductivity and *N*-type behaviour when a hot probe measurement was made.

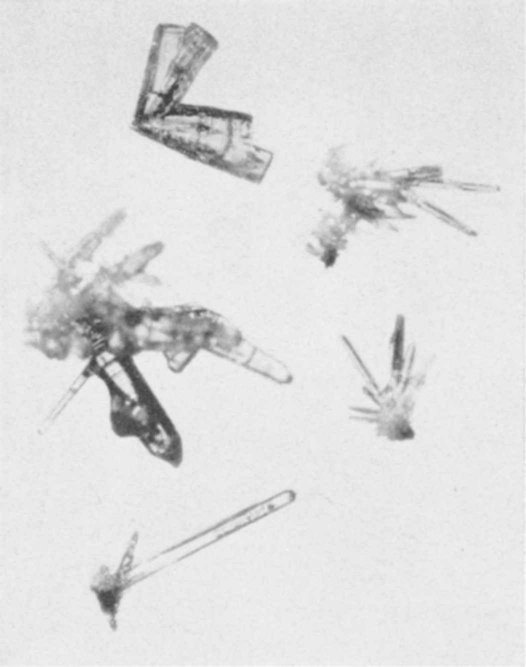

Figure 1 Single crystals of gallium nitride. Scale 1 in. = 5 mm.

X-ray diffraction patterns were obtained with CuKα-radiation using a Ni-filter. Both dark and colourless single crystals were examined along with the powder from which they were grown. The patterns obtained were identical and correspond to the data for gallium nitride in the ASTM file [10].

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References

1. E. KAUER and A. RABENAU, *Z. Naturforsch.* **12A** (1957) 942.
2. H. P. MARUSKA and J. J. TIETJEN, *Appl. Phys. Letters* **15** (1969) 327.
3. H. G. GRIMMEIS and H. KOELMANS, *Z. Naturforsch.* **14A** (1959) 264.
4. A. G. FISCHER, *Solid State Elect.* **2** (1961) 232.
5. W. C. JOHNSON, J. B. PARSONS, and M. C. CREW, *J. Phys. Chem.* **36** (1932) 2651.
6. A. RABENAU, in "Compound Semiconductors" edited by R. K. Willardson and H. L. Goering (Academic Press; New York, 1961) Ch. 19, Vol. I.
7. H. GRIMMEIS, R. GROTH, and J. MAAK, *Z. Naturforsch.* **15A** (1960) 799.

8. K. R. FAULKNER, B. J. ISHERWOOD, B. P. RICHARDS, I. H. SLOBEY, and D. K. WICKENDEN, *J. Mater. Sci.*, in press.
9. D. D. MANCHON, JR., A. S. BARKER, JR., P. J. DEAN, and R. B. ZETTERSTROM, *Solid State Comm.* (1970).
10. R. JUZA and H. HAHN, *Z. anorg. Chem.* **239** (1938) 282.

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R. B. ZETTERSTROM
Bell Telephone Laboratories Inc.
Murray Hill, New Jersey 07974, USA