A FEASIBILITY STUDY ON THE GROWTH OF BULK GaN SINGLE CRYSTALS. I.まとめ

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INTRODUCTION

The major goal of this investigation is to prepare bulk crystals
of gallium nitride. Since several investigators had used conventional
chemical transport reactions without major success, it was decided
to concentrate on methods involving the use of molten gallium.

Because of bureaucratic problems, the start of the second year
of funding was delayed but internal funding was used to maintain activity
at some reduced level in the interim period. This report includes the
findings of this interim period in addition to the first three months of
new funding.

The most important advance is the growth of crystals an
order of magnitude larger than reported previously. This advance hope-
fully will point the way towards a modified technique for preparing
large crystals.

EXPERIMENTAL RESULTS

A. Horizontal Crucible

Since the best results obtained during the first year of the pro-
gram involved the use of a horizontal furnace and a horizontal crucible
containing gallium or Ga/Bi alloy, recent work has mainly concen-
trated on this arrangement.

1. Attempts to Control Nucleation

The most serious experimental problem has been the difficulty in
restricting nucleation to a few crystals. Attempts were therefore made
to introduce a "cold spot" in the gallium at which nucleation would
occur preferentially.

"Electro-epitaxy" has been used successfully for the growth of
GaAs films from Ga solution (e.g., Imamura et al., 1978). The driving
force for crystallization in these experiments is two-fold: the electron
wind and the Peltier effect. The electron wind arises from the transfer
of momentum between the conduction electrons and solute atoms; this
will be negligible in GaN solutions since the solubility is so low. The Peltier effect is, however, independent of the solute concentration and it should be possible to induce nucleation on the anode where cooling occurs. The Peltier current was applied via a pair of graphite screws mounted in a fused quartz bridge across a quartz crucible. The temperature gradient in the furnace was adjusted to its lowest value and a current was applied between the electrodes while ammonia with hydrogen carrier gas was passed over the 4Ga:1Bi melt for about a week. These experiments were uniformly unsuccessful, even though the current density was as high as 10A/cm$^2$. In each case nucleation occurred on the surface of the liquid and on the walls of the crucible, apparently independently of the Peltier current.

A "cold finger" was therefore constructed using a graphite tube connected to a hollow graphite cone. Cooling was achieved by blowing the hydrogen plus ammonia gas through the tube to enter the furnace via a series of holes around the circumference of the cone. The cone was mounted so that its tip was just touching the surface of the melt. The gas was supplied at a rate of about 200 ml/min with an ammonia concentration of 2 X $10^{-3}$ with the melt maintained in a temperature gradient between 840° and 950°C. Experiments lasted from 6 to 10 days. Again these experiments were unsuccessful in that nucleation occurred over all the melt surface, apparently independent of the cold finger. These experiments were the first to give GaN in the form of needles, which had been reported previously by Ejder (1974) and Aoka and Tada (1979).

2. Use of Argon Carrier Gas

Hydrogen was used as carrier gas in all the early experiments following the experience of Logan and Thurmond (1972). This suffers from the disadvantages that it attacks the silica walls:

$$\text{SiO}_2 + H_2 \rightarrow H_2O + \text{SiO}$$

and that it retards the GaN formation reaction:

$$2\text{Ga} + 2\text{NH}_3 \neq 2\text{GaN} + 2H_2$$
A series of experiments was therefore performed with argon as carrier gas and with flowmeter, experiment duration, and temperature gradients similar to those used for hydrogen. The argon was purified by passing over Ti chips at about 700°C.

Argon was found to have an adverse effect on the growth morphology, since it led to the deposition of GaN (with Ga$_2$O$_3$, due to a cracked thermocouple sheath) only in the form of needles. Many of these needles were tipped with Ga, suggesting that they had grown by the VLS (vapor-liquid-solid) mechanism. Several needles were found to be hollow.

The needle morphology was attributed to a high supersaturation arising since, for the same flowmeter reading, the rate of flow of argon is substantially lower than that of hydrogen so that the partial pressure of NH$_3$ is higher. New flowmeters have been purchased so that these experiments may be repeated at the same partial pressure as in experiments using hydrogen.

3. **Nucleation on Graphite Wafers**

It had been found in earlier experiments that GaN nucleates relatively easily on graphite. Nucleation on graphite wafers was studied in one series of experiments, the subsidiary aim being to prepare coated wafers for use as source and seed in a vertical crucible. In these experiments hydrogen was used as carrier gas with the steepest temperature gradient, about 180°C across a six inch crucible. Pure Ga was used as solvent, the hot end of the crucible being at 1010°C and the cold end at about 825°C, with the experiment proceeding for about ten days.

The best results were obtained with three wafers located respectively at the hot end, center, and cold end, resting across the top of the crucible. These wafers restricted the tendency of gallium to creep toward the hot end of the furnace, this tendency depending on the high surface tension of gallium and its dependence on temperature and on the contacting surface. Crystals grown during this experiment are shown in Fig. 1, the largest being about 1½ mm in length.

Experiments aimed at a full understanding of the growth mechanism, and hence at designing new experiments to grow large crystals, are currently in progress.
Figure 1. Examples of GaN crystals grown in a horizontal temperature gradient. (Magnification: top 75X, bottom 50X)
B. Vertical Crucible

Experiments reported previously with the vertical crucible used a temperature gradient opposed to gravity so that slow transport of solute would occur purely by diffusion. Diffusional flow was found to be ineffective as a transporting agency so the temperature gradient was reversed in recent experiments. A temperature difference of 20-30°C was initially maintained across a 3½" column of gallium with GaN source material at the crucible base and a polycrystalline GaN seed at the colder end. Ammonia was maintained above the gallium at the equilibrium pressure. The experiment ran for 16 days, the result being that the source gained weight while the seed dissolved. A similar result was noted when the temperature difference was increased to 80°C.

It was concluded from these observations that GaN has a reciprocal solubility in Ga, at least over a temperature range around 900°C. This postulate will be tested in future experiments. In addition, apparatus to increase the rate of transport of solute by the use of mechanical stirring is under construction.

C. Decomposition of GaN

Groh et al. (1974) detected the decomposition of GaN at 980°C using thermogravimetry and at 800°C using changes in pressure in a high vacuum. In view of the importance of GaN decomposition for the design of experiments, we performed a similar study using the apparatus described in previous reports which was developed for measurements of the solubility of GaN in Ga.

It was found that the onset of decomposition occurred at about 750°C, approximately as reported by Groh et al. and that a progressive increase in decomposition rate occurred as the temperature was raised above this value. In addition, it was found that the onset of decomposition was substantially unaffected by the presence of gallium, so that no major difference could be detected between the decomposition of solid GaN and dissolved GaN.
D. Conclusions

In addition to problems of multinucleation, low solubility, and slow convection experienced in earlier experiments, it is postulated that the solubility of GaN in gallium follows a reciprocal temperature dependence. In spite of this handicap, it has been found possible to achieve conditions under which the nucleation of GaN is reduced in comparison to previous experiments and so to produce larger GaN crystals. The major aim of experiments in the near future will be to obtain a more complete understanding of the conditions required to produce large crystals of GaN.
REFERENCES


FISCAL STATUS FOR FIRST QUARTER  
July 2, 1979 through September 30, 1980  
Contract #N000-19-79-C-0327

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