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A FEASIBILITY STUDY ON THE GROWTH OF BULK GAN SINGLE CRYSTALS.(U)
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I. Introduction

The III-V semiconducting phosphides, arsenides and antimonides have been extensively investigated in recent years both with regard to single crystal growth and property evaluation. Relatively high quality material in the form of large single crystals and epitaxial layers can be routinely produced, and many of these materials have found use in device applications. The group III nitrides, on the other hand, have received little attention by comparison and techniques have not been sufficiently developed for the production of either adequate quality bulk single crystals or epitaxial layers.

Of the group III nitrides, GaN is of particular interest because it has a wide, direct bandgap (3.4 eV at 300°K) and is potentially useful as an electroluminescent material and injection laser. The possibility of extending the laser frequency with this material further into the visible (into the blue-green region) is very attractive for a number of underwater applications. While most III-V compounds crystallize with the diamond-cubic zincblende structure, GaN has the hexagonal wurtzite structure. It behaves electrically like the II-VI compounds, since it apparently exhibits only one conductivity type (n-type). The best synthesis technique for GaN, at present, involves the reaction of Ga or $GaC\ell$ with NH_3. Semi-insulating GaN epitaxial layers have been produced by doping with Zn; and a device made of a metal contact layer, a Zn doped GaN insulating layer, and an undoped n-type GaN layer, has shown d c electroluminescence.

Gallium nitride was first prepared(1) in 1932. Metallic Ga was contained in a quartz boat at 1000°C while NH_3 gas was passed over it. In this same study it was found that Ga did not react with N_2 gas even at high temperatures for long periods of time. The inert behavior of N_2 is probably the result of the great stability of the N-N bond ($\Delta H \approx 226$ Kcal/mole). To form GaN, therefore, it is necessary to provide a source of atomic nitrogen either decomposing N_2 or using NH_3 to provide a high N activity.

Efforts to produce GaN fall into two convenient categories:

(a) Reaction of Ga or its compounds with atomic nitrogen

(b) Reaction of Ga or its compounds with NH_3.

In case (a), several experiments have been reported. In the first(2), atomic nitrogen was prepared in an electric discharge and samples were contaminated from the electrodes. In another(3), atomic nitrogen was created in one arm of a Y-shaped tube in an rf gas discharge while Ga metal was vaporized in the second arm. Thin films of GaN were formed in the third arm on a heated substrate. Since the vapor pressure of Ga at the temperatures used was quite low, only very thin layers (1000Å) were produced. A third procedure involving reactive rf sputtering was also reported(4).

Reactions using NH_3 have also been reported. In the early variations, Ga compounds, such as $(NH_4)_3GaF_6$(5), Li_3GaN_2(6), $GaCl_3$(7), GaAs or GaP(8), and Ga_2O_3(9), were tried. The products were powders or tiny crystallites, usually contaminated with impurities from the starting materials.

It was not until 1969 that the first large area single crystal layers suitable for detailed investigations of material properties were grown. Films up to 100μ thick and 1 cm^2 were grown on sapphire and SiC substrates by an open-flow vapor growth process(10). This process involved the simultaneous transport of both GaCℓ (formed by the reaction of HCℓ and Ga upstream) and NH_3 separately to the furnace where the substrate was located. The formation of a GaN surface layer on the Ga source, a problem in most previous techniques, could thus be avoided. A similar growth process was described by Ilegems(11). Trimethylgallium was substituted for GaCℓ by Manasevit et al.(12). Logan and Thurmond(13) grew GaN hetero-epitaxial layers on sapphire substrates using Ga melts doped with Bi in an NH_3 atmosphere. The Bi enhanced the nucleation density so that individual crystals could coalesce into a continuous layer. A thermal gradient was used and the rate limiting step was the transport of N through the melt because of its low solubility.

The preparative techniques currently used for producing single crystals or epitaxial layers of GaN have not yielded very satisfactory results. Small mm size crystallites are the best that investigators have been able to accomplish with respect to the growth of bulk crystals,while marginal hetero-epitaxial layers on sapphire substrates have been prepared such that preliminary property measurements could be made.

The major reason for the difficulty in producing large GaN single crystals is the thermal instability of GaN at elevated temperature coupled with a low solubility of GaN in Ga melts (10^{-5} mole fraction at 1150°C). Lorenz and Binkowski(9) observed the evolution of N_2 gas from GaN heated to temperatures as low as 600°C. Thurmond and Logan(14) found that at 800°C the equilibrium pressure of N_2 over GaN(s)-Ga(l) is greater than one atmosphere and rises to 100,000 atm at 1700°C.

Under NH_3, however, the N_2 pressure is not one atmosphere at 800°C, and Maruska and Tietjen(10) reported growing GaN at 825°C with an NH_3 partial pressure of 0.14 atm (H_2 partial pressure 0.86 atm). It might be possible to extend the usefulness of this growth technique to the growth of large single crystals.

The initial year of the program consisted of two principal phases. The first was an analytical review and theoretical analyses of existing crystal growth procedures and of thermodynamic data relevant to possible new methods. The second was a concurrent experimental program designed to focus on two methods, (1) solution growth (Ga solvent) in a temperature gradient and (2) growth from solutions with enhanced nitrogen solubility.

II. Results of the Initial Program

A. Experimental

1. Horizontal Temperature Gradient Transport Method: Using the experimental arrangement of Fig. 1, gallium or a gallium bismuth alloy was contained in a 6" long, glassy-carbon coated crucible in a flowing NH_3/H_2 gas stream and with a 100°C temperature difference maintained between the ends of the crucible while the hot end was held at various temperatures. Very encouraging results have been obtained with this procedure. GaN was synthesized on the surface of the melt, on the crucible walls, in the bulk gallium and on a sapphire substrate located partly inside and partly outside of the melt. The region of sapphire which was outside the melt had been covered by a thicker deposit than the portion below the melt surface. The GaN coating at the sapphire/melt interface was very inhomogeneous,

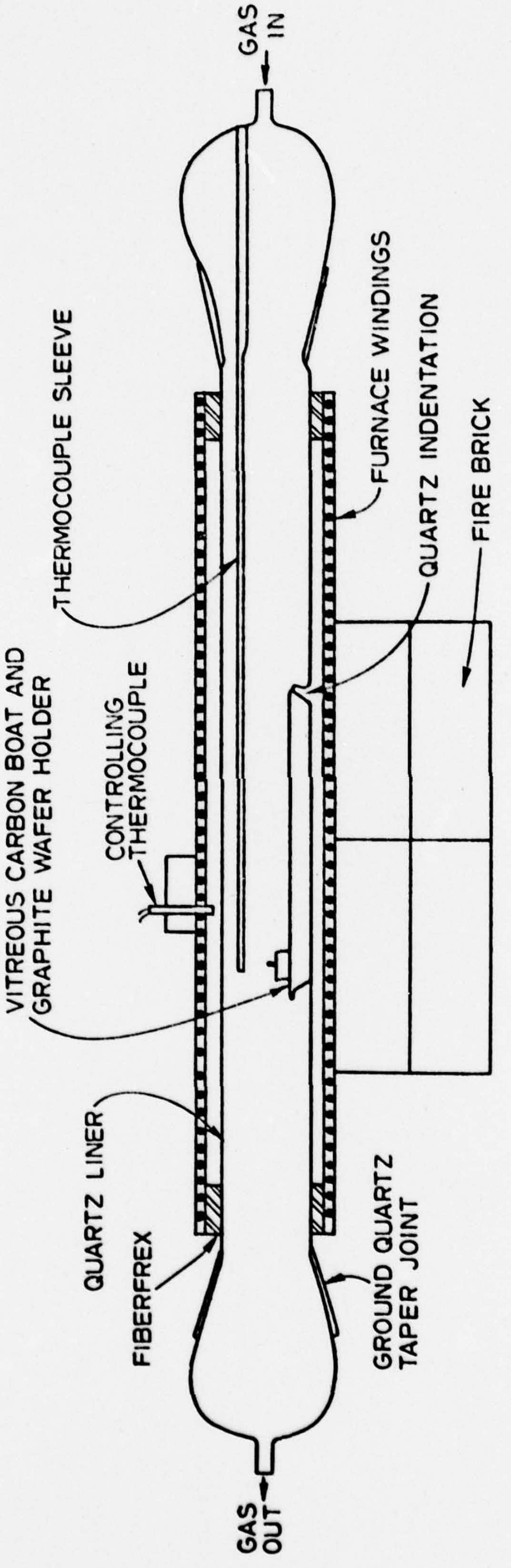

FIGURE 1. Horizontal temperature gradient transport system.

denoting poor wetting conditions and indicating that sapphire is not a good substrate for the seeding of GaN crystals.

The mass of GaN crystals harvested and the maximum crystal size observed in individual 6-day runs, with the top crucible temperature between $900^{\circ}C$ and $1050^{\circ}C$, is presented in Fig. 2. The mass yield of crystals grew to several grams in the $950^{\circ}C$ - $1050^{\circ}C$ range, which indicates substantial transport rates in this sytem, a necessary precursor for the generation of large single crystals. This mass yield levels at the higher temperature, presumably as a result of sublimation or decomposition of the GaN(s) formed. The maximum crystal diameter, D_{Max}, grew steadily as the growth temperature was increased. These crystals were always found in the high temperature region of the melt indicating that one should prepare the crystals at the highest possible temperatures subject to one's ability to control the sublimation/decomposition reaction. A photograph of the best crystals obtained to date is given in Fig. 3.

At the different growth temperatures, GaN powder was also located on the silica tube surrounding the boat indicating either reaction between ammonia and gallium vapor or evaporation and condensation from the melt-grown solid GaN.

2. <u>Vertical Temperature Gradient Transport Method</u>: Figure 4 illustrates the experimental apparatus used with the nitrogen being supplied from ammonia gas in a concentration of about 2×10^{-3} in hydrogen flowing at about 200 ml/min. A temperature difference $\Delta T \sim 100^{\circ}C$ was maintained across a 2-3 inch column of gallium with the gas being supplied ~ 0.5 inches

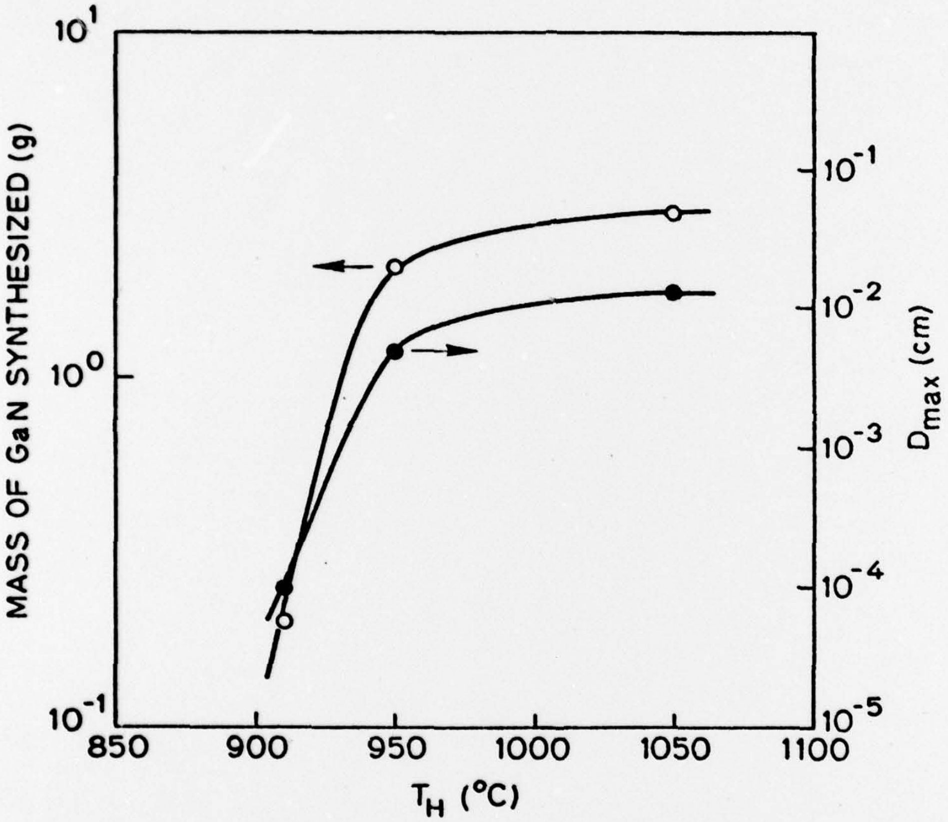

FIGURE 2. Mass of GaN and size of largest crystals (D_{max}) versus the temperature of the hot end of the crucible.

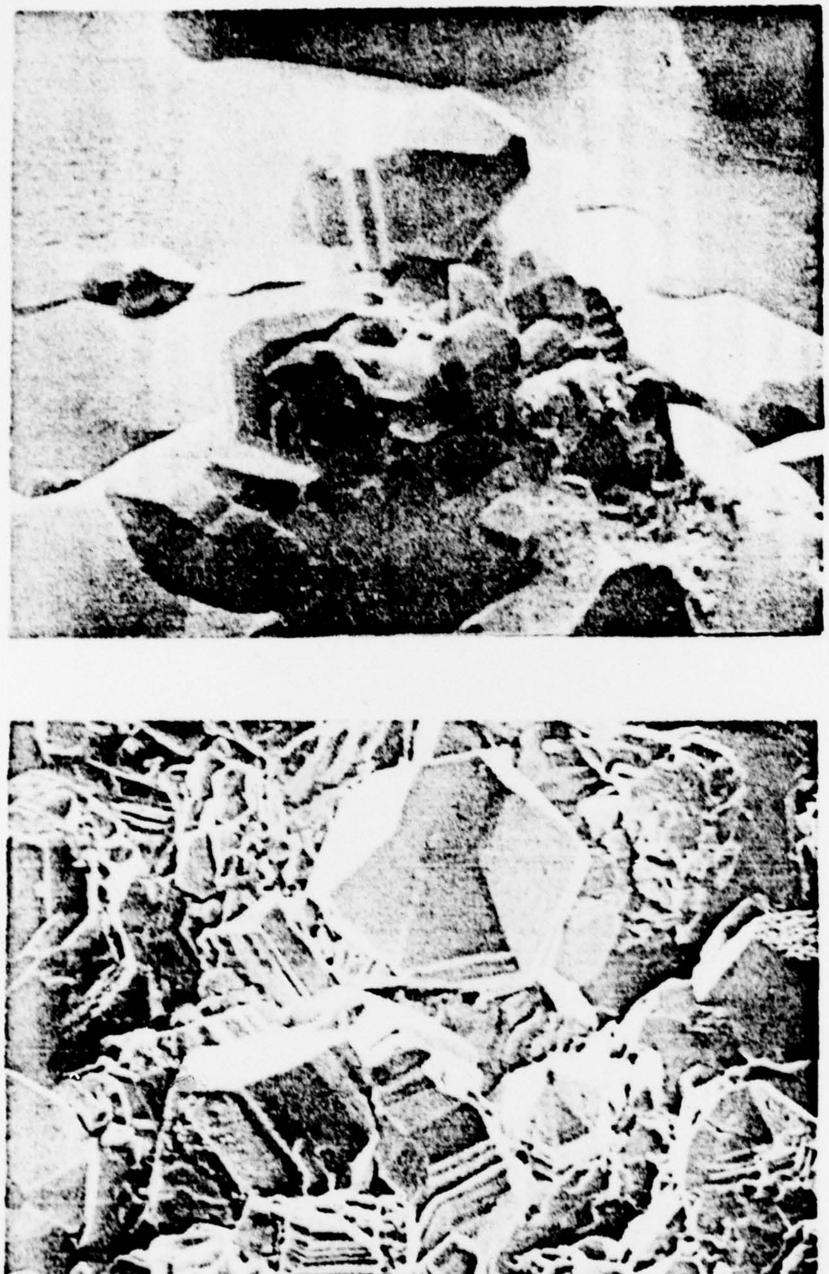

Fig. 3. Examples of GaN crystals grown on the surface of the melt in the horizontal gradient transport arrangement (800X).

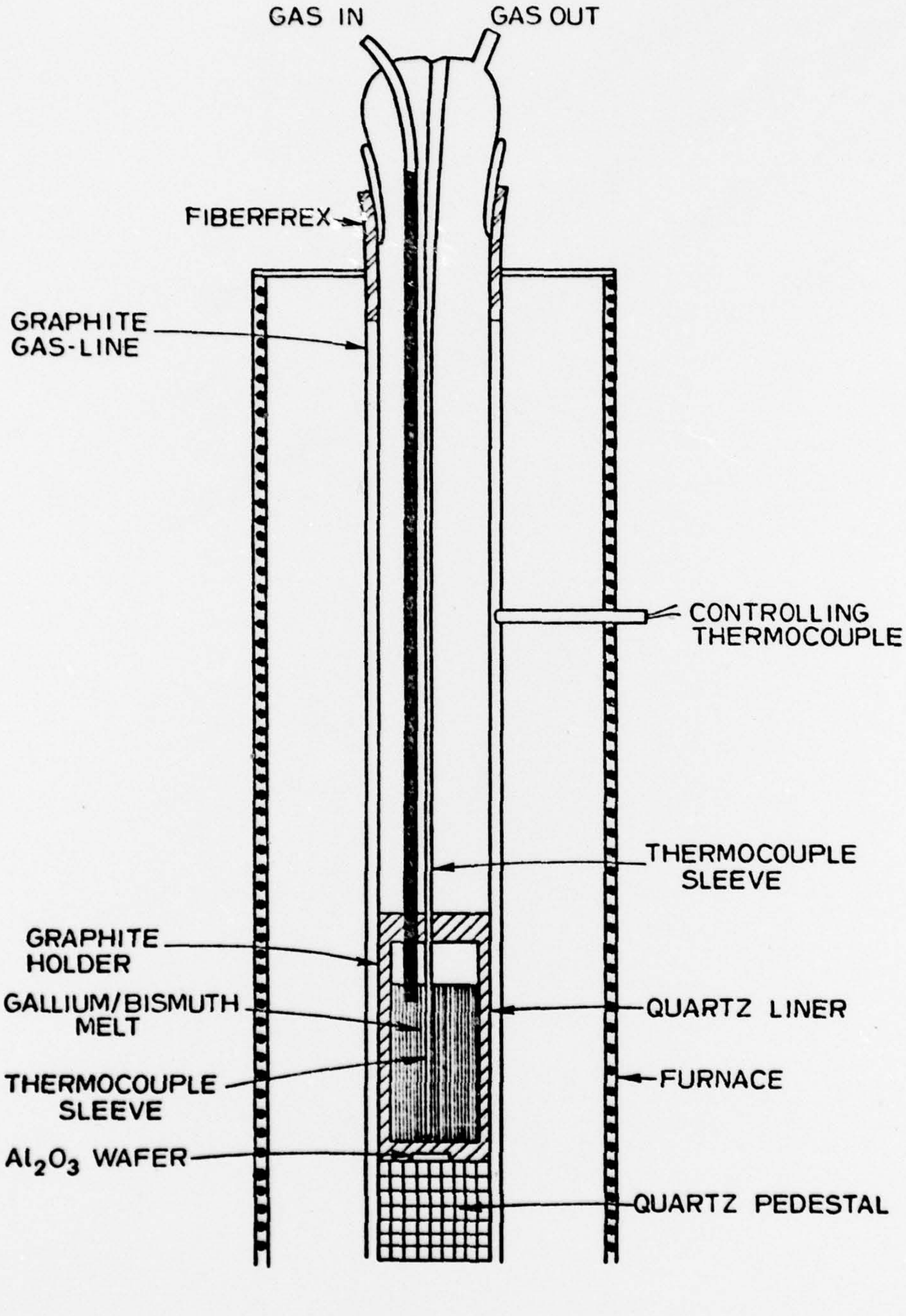

FIGURE 4. Vertical temperature gradient transport system.

below the liquid surface. This provided both stirring of the fluid plus the source of N. A sapphire substrate wafer was located at the bottom of the crucible. The top surface of the crucible was the hottest temperature.

The initial results have been disappointing and, with an SiO_2 crucible, the main element transported and deposited on the sapphire substrate was silicon ($H_2 + SiO_2 \rightarrow H_2O + SiO$). Replacing the SiO_2 crucible and tubing with graphite has substantially reduced, but not completely eliminated, the silicon contamination. Only a few milligrams of GaN was observed to form on the graphite crucible walls and none on the sapphire substrate over a two-week run. The GaN was not densely concentrated at the upper regions of the crucible and the mass gradually decreased to zero above the bottom of the crucible. This was very fine grain material. The transport rate seemed to have been very limited in this setup, or else the supply between the gas and the liquid was somehow limiting the situation in a non-obvious way.

3. Nitrogen Solubility Studies: Figure 5 represents the apparatus used in these studies. In operation, a carrier gas containing ammonia at a pressure about twice the equilibrium value is passed over gallium at constant temperature for 1 hour. The furnace is then lowered to quench the gallium, the gas supply is closed off and the space above the sample is evacuated. The vacuum valve is closed and the furnace raised around the gallium again to heat it to 1000°C. The pressure is measured continuously for about 1 hour using a thermocouple gauge. This should be long enough to establish a constant pressure due to decomposition of the nitride in the

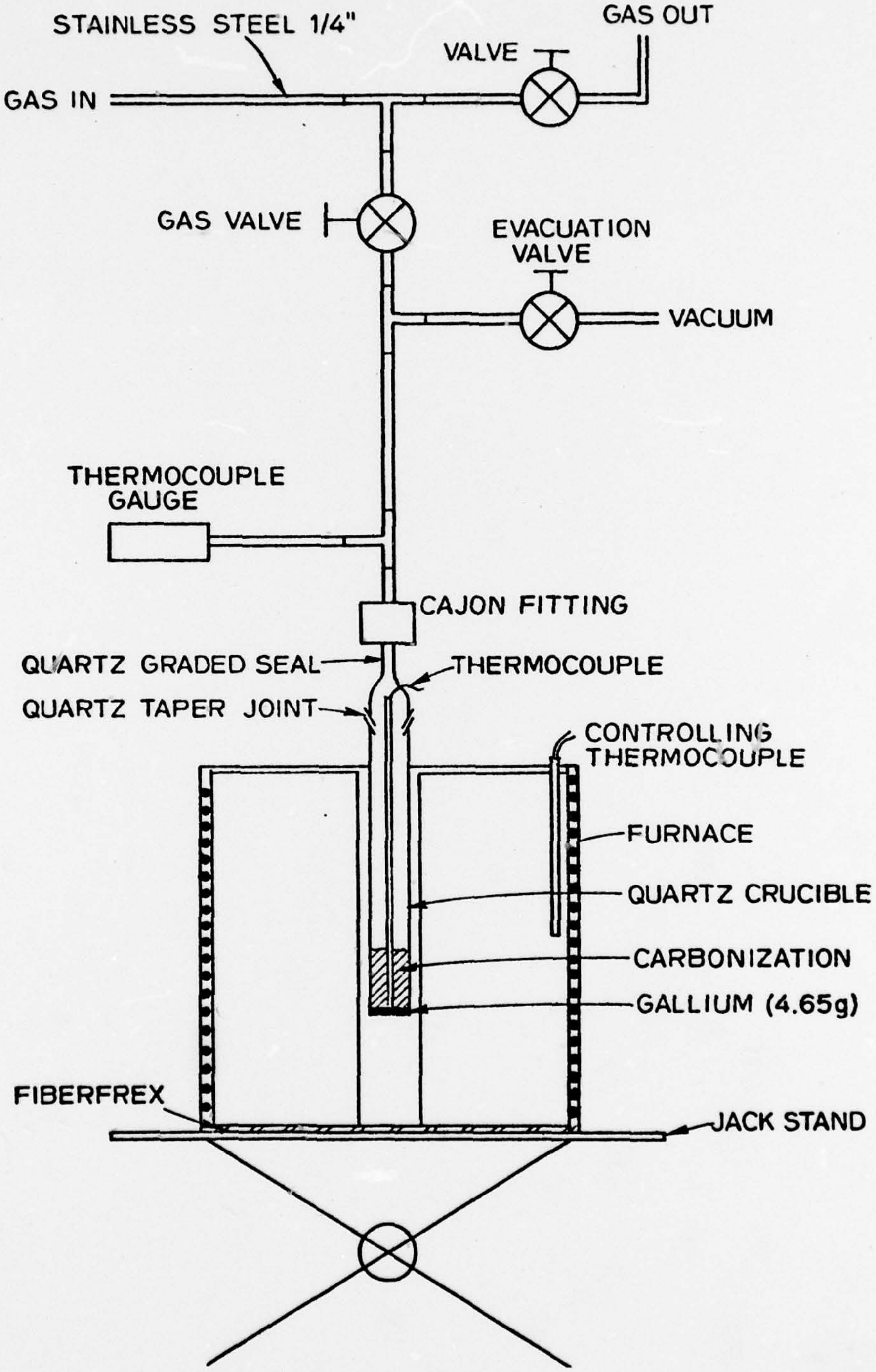

FIGURE 5. Nitrogen solubility apparatus.

gallium plus desorption of gases adsorbed on the walls or dissolved in the gallium. The process is then repeated to establish the "base line" pressure rise due to virtual leaks in the system.

Results from this procedure indicate a solubility of ~ 10^{-5} gms GaN per gm of gallium at 950°C, which is the proper range based upon published data. However, the system is not yet working satisfactorily and the possibility of residual leaks has not yet been totally eliminated.

B. Theoretical

1. Thermodynamics and Kinetics: By increasing the pressure of H_2 and NH_3 over the surface of a gallium melt, while growing a crystal at a submerged location and at a lower temperature, the activity of N_2 over the melt is given from

$$NH_3(g) \rightleftarrows \tfrac{1}{2} N_2(g) + \tfrac{3}{2} H_2(g) \qquad (1)$$

by

$$a_{N_2}^{1/2}(g) = K\, P_{NH_3}/P_{H_2}^{3/2} \qquad (2)$$

where K is about 3×10^3 at 825°C. From the reaction

$$\tfrac{1}{2} N_2(g) \rightleftarrows N(g) \qquad (3)$$

we have

$$N(g) \;=\; (K')^{\frac{1}{2}}\, K\, P_{NH_3}/P_{H_2}^{3/2} \;\sim\; 3 \times 10^{-4}\; P_{NH_3}/P_{H_2}^{3/2} \tag{4}$$

where K' is about 10^{-14} at 825°C. Using Sievert's law, the activity of N in the melt is found to be

$$a_N(\ell) \;=\; K_\ell^N\, K'^{\frac{1}{2}}\, K\, P_{NH_3}/P_{H_2}^{3/2} \tag{5}$$

Assuming K_ℓ^N for the partitioning of N between the gas and the liquid state to be $\sim 10^{-1} - 10^{-2}$, at 1 atm total pressure, eq. 5 predicts a value for $C_N \sim 10^{-5} - 10^{-6}$ in the melt. This is in accord with the experimental estimates. We can thus conclude that the thermodynamic understanding of the system is reasonably well in hand.

On the kinetic side, if we assume $C_{N\infty} \sim 10^{-5} - 10^{-6}$ in the melt, a thermally-driven natural convection producing a solute boundary layer thickness at a crystal interface of $\delta \sim 10^{-1} - 10^{-2}$ cm and an equilibrium interface concentration $C_{N\,eq} \sim 10^{-1}\, C_{N\infty}$, then the crystal growth velocity, V, is given by

$$V \approx D\,\frac{(C_{N\infty} - C_{N\,eq})}{\delta} \;\sim\; \frac{10^{-5}\,(10^{-5} - 10^{-6})}{(10^{-1} - 10^{-2})} \;\sim\; 10^{-8} - 10^{-10}\ \text{cm/sec} \tag{6}$$

Thus, $V \sim 0.1 - 10$ microns/day, which is the observed experimental range. If interface attachment kinetics are also limiting the growth, then we have

$$V \approx D \frac{(C_{N\infty} - C_{N\,eq} - \Delta C_K)}{\delta} \qquad (7)$$

which may yield an order of magnitude smaller V than that given by eq. 6. As the growth temperature increases, ΔC_K decreases and V approaches the eq. 6 value. With controlled stirring and a single crystal seed, δ could be reduced to ~ 10^{-3} cm with a subsequent increase of V to ~ 100 microns/day. Any further increase of V can only be gained by an increase in $C_{N\infty}$.

2. Methods for Increasing Solubility: Three avenues for increasing the activity of N in Ga melts have been proposed, (a) the addition of a ternary constitutent to the Ga melt which lowers $a_N(\ell)$ so that the solubility for a given $a_N(g)$ will increase; i.e., k_ℓ^N in eq. 5 will increase, (b) manipulate the gas phase using various modes of carefully controlled electrical discharge so as to shift the ratio a_N/a_{N_2} in the gas phase at the Ga melt surface with a subsequent increase in the effective value of K' in eq. 5. In addition, one might expect that different excited states of N should alter k_ℓ^N, and (c) apply a voltage to the Ga surface so as to shift its isoelectric point and thus alter the solubility of N in the interface layer.

The first avenue has led to the development of a technique (see section A.3) for measuring the solubility of nitrogen in gallium. However, it is not yet in a satisfactory condition and no data has been gathered on possible candidates. For the same reason, the discharge techniques have not yet been explored experimentally. However, theoretical evaluation indicates that K' in eq. 5 can be increased by many orders of magnitude so that $C_{N\infty}$ may be increased by at least two orders of magnitude. This would, indeed, allow macroscopic size GaN crystals to be grown. From theoretical consideration of the third avenue, the surface concentration of an electrolyte species can be increased or decreased by an order of magnitude in an aqueous system by relatively small changes in the surface voltage relative to the isoelectric point. Similar behavior is expected for a gallium surface.

3. Evaluation of Additional Needs for Obtaining Large Crystals: The two additional problems needing attention are (a) nucleation of new crystals during the growth of seeds and (b) decomposition of GaN crystals at the higher temperatures. The experimental data clearly indicates that the GaN crystals readily nucleate at small suspersaturations. If we call this supersaturation ΔC^*, then the growth temperature, relative to the bulk liquid temperature, must be reduced until $(C_{N\infty} - C_{N\ eq} - \Delta C_K)$ in eq. 7 is less than ΔC^*. Thus, V will be reduced unless δ can be reduced correspondingly. Alternatively, and/or additionally, one may wish to use electromigration techniques to augment the transport of N to the seed crystal.

Preliminary analysis of the decomposition reaction suggests that it may actually be a sublimation of the GaN species. If so, this could be controlled by the addition of a controlled pressure of GaN vapor species from an alternate source. Mass spectrographic analysis plus further theoretical exploration is needed to evaluate the feasibility of pushing the critical sublimation condition to significantly higher temperatures.

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