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[54] **GROWTH OF GALLIUM NITRIDE CRYSTALS**

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[52] **U.S. Cl.** ..... **423/409,** 252/62.3 GA

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[58] **Field of Search** ..... 423/409; 75/134 T; 252/62.3 GA

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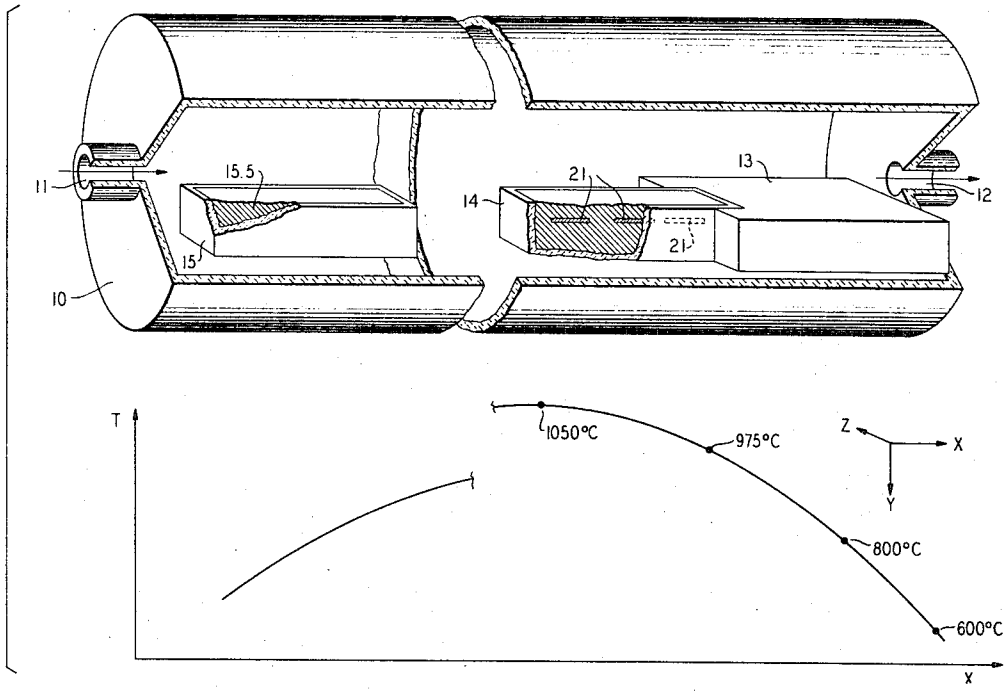
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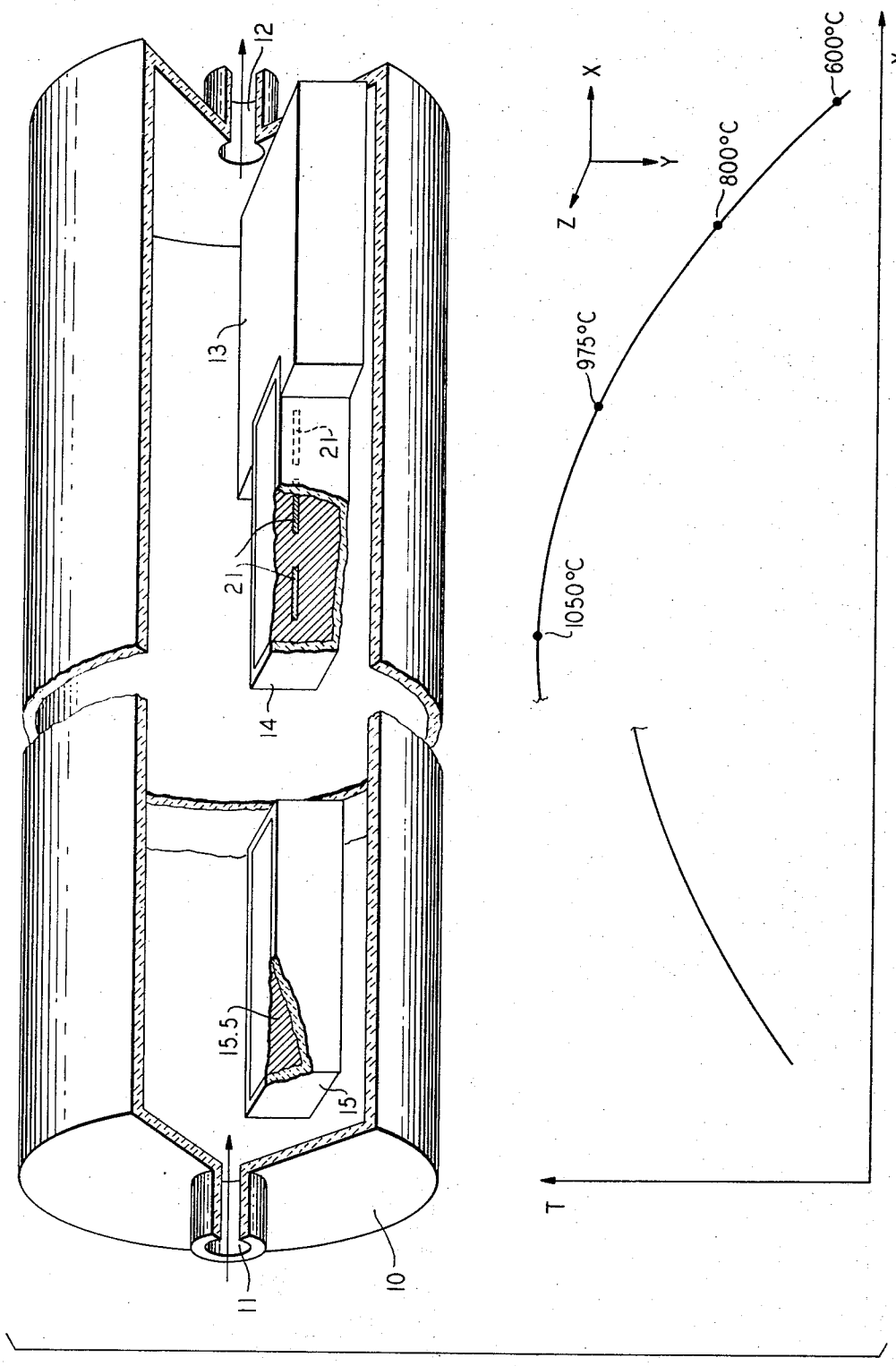
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[57] **ABSTRACT**

The size and photoluminescent efficiency of crystals of gallium nitride, grown in a solution of molten gallium and bismuth, are improved by maintaining the partial pressure of ammonia vapor in a hydrogen gas atmosphere flowing above the solution at a value which is, at most, about an order of magnitude greater than the "equilibrium pressure" of formation vs. decomposition of gallium nitride. The photoluminescent efficiency of a blue band, whose energy is centered around 4,350 angstroms, emitted by such gallium nitride crystals is also improved by introducing zinc vapor into the carrier gas.

10 Claims, 1 Drawing Figure




12
13
21'
21
14
15.5
15
11
10
X
Y
Z
600°C
800°C
975°C
1050°C
X
T

GROWTH OF GALLIUM NITRIDE CRYSTALS

FIELD OF THE INVENTION

This invention relates to methods for growing luminescent crystals and, more particularly, to a technique for the growth of photoluminescent gallium nitride crystals.

BACKGROUND OF THE INVENTION

The development of technologies using optical displays and optical sources, such as the computer and communication technologies, has necessitated a search for light-emitting devices which can emit light at certain desired visible wavelengths or combinations thereof (colors). It has long been known that semiconductive gallium nitride can emit visible blue light when irradiated with the invisible ultraviolet. Thus, blue photoluminescent semiconductor devices, that is, devices emitting blue light under excitation by an optical source, can be made using semiconductive gallium nitride crystals as the photoluminescent material ("phosphor").

It has also been known in the prior art that gallium nitride crystals can be formed from molten gallium by passing ammonia at atmospheric pressure over the molten gallium at a temperature of the order of 1,000° C. See: W. C. Johnson et al., *Journal of Physical Chemistry*, Vol. 36, p. 2651 (1932). However, crystals of gallium nitride formed by such methods are limited to a particle size of about a micron. See: H. G. Grimmeiss, *Journal Applied Physics*, Vol. 41, p. 4054 (1960). Crystals of such a small size are not very useful for devices.

On the other hand, in the growth of gallium phosphide crystals from gallium solutions, an improvement in crystal size has been reported by adding bismuth to the molten gallium growth solution, in order to inhibit the formation of spurious gallium phosphide crystal nuclei and thereby to allow more raw material to be available for the growth of fewer but larger gallium phosphide crystals. See: F. A. Trumbore et al., *Applied Physics Letters*, Vol. 9, p. 4 (1966). It has been thought in the art, however, that any growth of gallium nitride crystals from a solution, similar to that just mentioned for gallium phosphide, cannot possibly yield reasonably large crystals, since the amount of gallium nitride which can be dissolved in the solution was believed to be too small. It would therefore be desirable to have available a solution growth method for growing gallium nitride crystals of considerably larger size than previously obtained.

SUMMARY OF THE INVENTION

We have discovered a method by which gallium nitride crystals can be grown in solution to a crystal size of the order of 1 centimeter square by several mils thick or more, on a substrate such as sapphire. In order to achieve this relatively large size growth, we have utilized a modified solution growth technique in which a gallium nitride crystal is grown on the substrate immersed in a heated growth solution of molten gallium and bismuth, in the presence of ammonia vapor above the solution in a furnace. We have found that it is important that the rate of reaction of ammonia with gallium be slowed by maintaining the partial pressure of the ammonia vapor above the solution at a value which

is much lower than used in the prior art. The main consequence of this slower reaction rate is the elimination of the undesired spreading of solution which occurs at higher ammonia vapor pressures, whereby the liquid gallium flows up and over the walls of the container ("boat") into the furnace.

In setting forth the range of the partial pressure of ammonia vapor in hydrogen gas to be used in accordance with this invention, it is convenient to define this range in terms of the "equilibrium pressure" at which the competing processes, of formation of gallium nitride from gallium vs. decomposition of gallium nitride by hydrogen, are characterized by equal rates. In these terms, we have found that the partial pressure of ammonia vapor should be maintained in the range from slightly greater than this equilibrium pressure to less than about five, and at most ten times this equilibrium pressure, and preferably about twice this equilibrium pressure.

In a specific embodiment of the invention, ammonia vapor in a carrier gas, hydrogen, is passed over the surface of a growth solution of gallium and bismuth at an elevated temperature. Advantageously, zinc vapor is also introduced into the carrier gas, in order to incorporate zinc as an impurity into the gallium nitride crystals and thereby to improve the photoluminescent efficiency. Immersed in the growth solution are substrates, such as sapphire, for the epitaxial crystal growth of gallium nitride. A temperature gradient is maintained across the surface of the growth solution, such that the upstream end of the growth solution with respect to the flowing carrier gas is at a somewhat higher temperature than the downstream end. Thereby, while nitrogen from the ammonia vapor will continuously dissolve into the growth solution, mainly at the higher temperature (upstream) region of the solution, a growth of gallium nitride crystals on the substrates will tend to occur in the lower temperature (downstream) region. This crystal growth thus occurs in a controllable fashion in which the partial pressure of ammonia vapor in the carrier gas is continuously maintained at a suitable value as set forth previously.

Crystals of gallium nitride grown in accordance with our invention have exhibited as much as 25 percent (photoluminescent efficiency) conversion at room temperature of ultraviolet light from a nitrogen gas laser (3,500 angstroms) into visible blue light (ranging from about 3,800 to 6,200 angstroms). Such crystals are also expected to be useful as the lasing material in solid state laser sources of blue light.

BRIEF DESCRIPTION OF THE DRAWING

This invention can be better understood from the following detailed description when read in conjunction with the drawing in which the FIGURE shows gallium nitride crystals being grown in a furnace, partly in perspective, in accordance with a specific embodiment of the invention.

DETAILED DESCRIPTION

As shown in the FIGURE, a furnace **10** is maintained at a temperature profile indicated immediately beneath it, by conventional heating means (not shown). It should be understood that the precise temperatures indicated in the FIGURE are not crucial, but can vary over wide ranges so long as the overall general shape of the profile is maintained. The furnace **10** has an inlet

11 and an outlet 12 for the flow of ambient gas. At the inlet, this gas is composed of ammonia vapor in the carrier gas, hydrogen, at a total pressure of 1 atmosphere. Toward the downstream end of the furnace 10 is located a carbon heat sink 13 partially surrounding a growth boat 14; whereas toward the upstream of this furnace 10 is located a zinc dopant boat 15. In this way, doping impurities of zinc are vaporized from the dopant boat 15 and then flow with the ambient gas over the growth boat 14.

By way of illustration only, typical dimensions for the various elements and their mutual spacing are as follows. The growth boat 14 is about three inches long in the x direction, one-half inch wide in the z direction, and one-half inch deep in the y direction. The heat sink 13 is about four inches long in the x direction and is about three-quarter inch wide in the z direction, and has a recess about one inch long in the x direction and one-half inch wide in the z direction, in order to accommodate a portion of the growth boat 14 in close contact therewith. About 12 inches to the left-hand side of the growth boat 14 and at a distance of about two inches from the inlet side of the furnace 10, the dopant boat 15 is located. This dopant boat 15 is about three inches long in the x direction, one-half inch wide in the z direction, and one-half inch deep in the y direction. The furnace 10 is in the form of a cylinder having a cross-section diameter of about seven-eighths inch. This furnace 10, as well as the growth boat 14 and the dopant boat 15, can be made of pyrolitic carbon or quartz, for example.

In order to grow gallium nitride crystals, a growth solution alloy of gallium and bismuth is introduced into the growth boat 14 to fill the boat typically about nine-tenths full. Then, sapphire substrates oriented typically (0001) are placed on the top surface of the solution in the growth boat 14. Next, these substrates 21 are covered with more solution of gallium and bismuth so that the growth solution in the growth boat 14 fills this boat, thereby leaving these substrates 21 suspended in the growth solution. Each of these substrates 21 has a cross section of approximately 1 cm^2 in the xz plane and advantageously has been coated with a predeposit of a gallium nitride epitaxial layer on the surface where gallium nitride is to be grown. For example, well-known vapor phase reactions of the prior art can be used for this predeposit, typically three microns thick. However, it should be understood that this pre-deposit is not necessary, but such a predeposit is useful in nucleating growth so that a gallium nitride crystal is grown over the entire predeposited region of the substrate rather than a major fraction thereof.

The temperature profile indicated in the temperature profile in the drawing is then established in which the average temperature of the growth alloy is in the range of about 850° C. to 1,050° C., typically about 1,000° C. The left-hand end of the growth boat 14 is maintained at a temperature gradient corresponding to a temperature difference of about 75° C. over a distance of about 3 inches in the x direction (allowing for the 1 inch recess in the carbon heat sink 13). This temperature difference is not critical and can vary by about 50° C., and thus the corresponding temperature gradient can be in the range of about 17° C. to 33° C. per inch. The dopant boat 15 is maintained at a temperature in the range of about 500° C. to about 825° C. and contains molten zinc 15.5. Thereby, zinc vapor at partial pressures of between approximately 0.001 and 0.1 atmosphere is introduced into the carrier gas of hydrogen containing ammonia vapor, flowing from the inlet 11. The rate of gas flow from inlet 11 to outlet 12 is maintained at a rate of typically 140 cm^3 per minute. With the temperature profile maintained as indicated in the FIGURE, gallium nitride then grows a single crystal layer on the sapphire substrates 21 to a thickness of a few mils in a time period of about 16 hours.

The solution in the growth boat 14 contains gallium and bismuth typically in a 50/50 ratio by atomic percent. For this 50/50 mixture, advantageously the partial pressure of ammonia at the inlet 11 is adjusted to be in the range of about 3×10^{-3} and 1×10^{-2} atmospheres, typically 6×10^{-3} atmospheres. However, a different ratio of bismuth to gallium also can be used in this invention. In particular, this ratio can be as high as about 90 atomic percent bismuth in combination with using a somewhat higher partial pressure of ammonia (0.03 atmosphere) in the hydrogen gas flowing into the inlet pipe 11. Likewise, as little as 30 atomic percent bismuth in gallium solution may be used in combination with a partial pressure of ammonia of about 4×10^{-3} atmosphere in the flowing hydrogen gas.

It should be recognized that higher concentrations of bismuth in the gallium solution in the boat 14 correspond to a greater ammonia partial pressure in the carrier gas flowing from the inlet pipe 11 to the outlet pipe 12, in order to maintain the same conditions relative to equilibrium conditions (rate of decomposition in hydrogen equal to the rate of formation from gallium of gallium nitride), according to the well-known stoichiometric relations:

$$2\ NH_3 + 2\ Ga \rightarrow 2\ GaN + 3H_2.$$

Gallium nitride semiconductor crystals grown by the above-described method are characterized by n-type conductivity. Utilizing these crystals grown by the above-described method, conversion of at least 25 percent of the output radiation of a nitrogen gas laser (about 3,500 A) into visible blue light has been achieved.

While this invention has been described in detail in terms of a specific embodiment, various modifications may be made without departing from the scope of this invention. For example, inhibitors other than bismuth can be used in the molten gallium growth solution, such as antimony, lead, tin, thallium, and indium. In addition, instead of the use of sapphire substrate, other substrates can be used, such as silicon carbide or other substrates with lattice structures compatible with the growth of gallium nitride. Moreover, it should be recognized by the skilled worker that as there becomes available in the art a method for making p-type gallium nitride crystals, then such crystals could be used as the substrate for making p-n junctions by the above-described method in accordance with the invention. Such p-n junctions would be especially useful for making electroluminescent devices, that is, light-emitting diodes excited by electrical current. Alternatively, various surface barriers, such as Schottky barriers formed by such metals as gold or aluminum, on the n-type gallium nitride crystals grown by the method of this invention, can be utilized instead of p-n junctions for the fabrication of electroluminescent devices.

What is claimed is:

1. A method of growing a crystal of gallium nitride which comprises the steps of:
   a. placing a substrate of sapphire in a solution comprising molten gallium which contains bismuth as an inhibitor of the growth of gallium nitride, at a temperature in the range of between about 850°C and about 1,050°C; and
   b. flowing a gas mixture comprising ammonia vapor in hydrogen gas across the exposed surface of the solution, said ammonia vapor being maintained at a predetermined partial pressure which is no more than about an order of magnitude greater than the equilibrium partial pressure of ammonia vapor with respect to the formation vs. decomposition of gallium nitride in said solution, whereby a single crystal layer of gallium nitride is grown on the substrate in the solution.

2. The method recited in claim 1 in which the composition of the solution is in the range between about 10 atomic percent to about 90 atomic percent bismuth in gallium, and the partial pressure of ammonia vapor does not exceed 0.03.

3. The method recited in claim 1 in which a temperature gradient is established across the exposed surface of the solution, said temperature gradient being in the range of about 17° to about 33° C. per inch.

4. The method recited in claim 1 in which the said partial pressure of the ammonia vapor is no more than about five times the said equilibrium partial pressure.

5. The method recited in claim 4 in which the partial pressure of ammonia vapor is about twice the equilibrium pressure.

6. The method recited in claim 1 in which the substrate has a predeposit thereon of epitaxial gallium nitride.

7. The method recited in claim 1 which further includes introducing zinc vapor into the gas mixture.

8. The method recited in claim 7 in which the partial pressure of zinc vapor is of the order of 0.1 atmosphere.

9. A method of growing a crystal of gallium nitride which comprises:
   a. placing a substrate of sapphire in a solution comprising molten gallium and an inhibitor of the growth of gallium nitride, at a temperature in the range of between about 850°C and about 1,050°C, said inhibitor being essentially a member of the group consisting of bismuth, antimony, tin, thallium and indium;
   b. flowing a gas mixture containing ammonia vapor in hydrogen across the exposed surface of the solution, said ammonia vapor being at a predetermined partial pressure no more than five times the equilibrium pressure for the formation vs. decomposition of gallium nitride, whereby a single crystal layer of gallium nitride is grown on the substrate in the solution.

10. The method of claim 9 in which a temperature gradient is maintained in the range of about 17° to about 33°C per inch across the exposed surface of the solution during the step of flowing the gas mixture.

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