United States Patent

Panish et al.

[15] **3,677,228**

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[54] CRYSTAL GROWTH APPARATUS

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Related U.S. Application Data

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[52] **U.S. Cl.**.....**118/422,** 118/50, 23/273 SP

[51] **Int. Cl.**.....**B05c 3/00,** B01d 9/00

[58] **Field of Search**.....23/273 SP, 301 SP, 273 R, 294; 118/422, 423, 425; 15/236 R

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[57] **ABSTRACT**

A crystal growth apparatus suitable for preparing epitaxial films of Group III(a) – V(a) compounds by tipping techniques is described. The novel apparatus includes means for removing deleterious oxides from the surface of source solutions prior to the deposition thereon of seed crystals.

1 Claim, 6 Drawing Figures

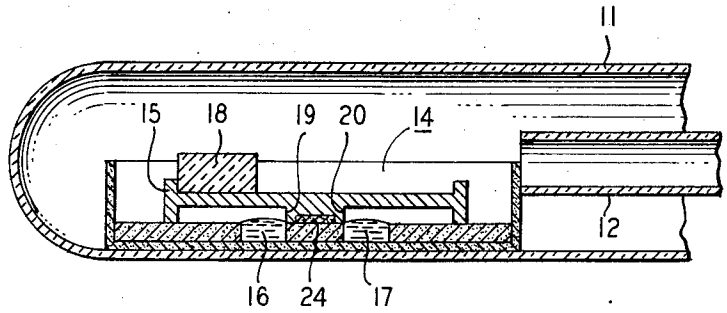


FIG. 1

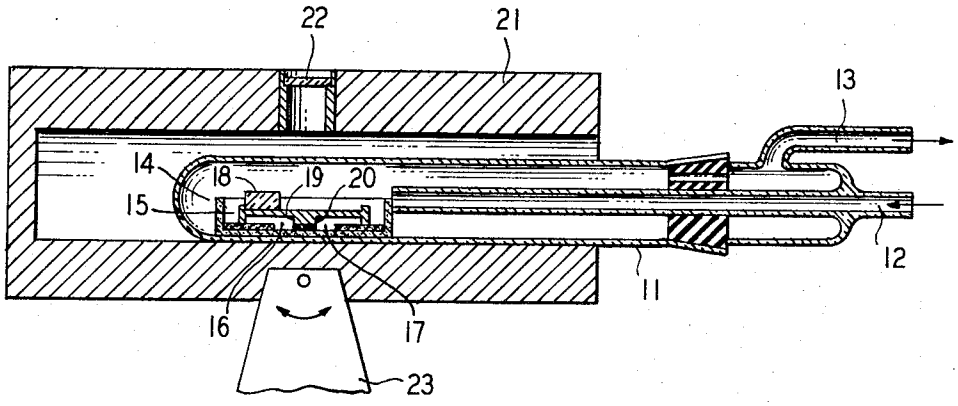


FIG. 2

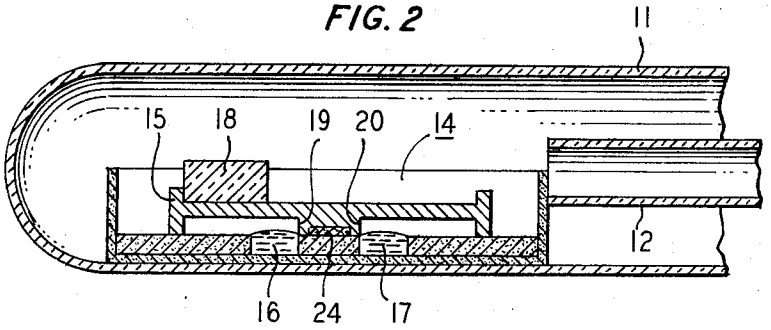


FIG. 3A

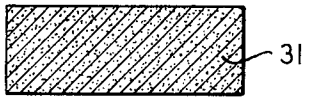


FIG. 3B

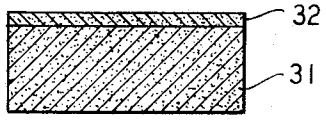


FIG. 3C

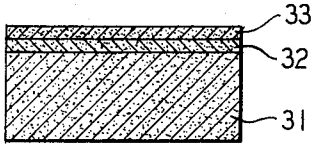
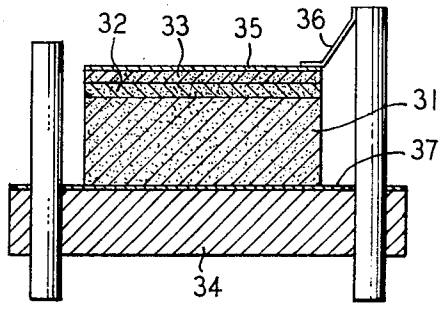


FIG. 3D



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CRYSTAL GROWTH APPARATUS

This application is a division of copending application, Ser. No. 727,927, filed May 9, 1968.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a crystal growth apparatus. More particularly, the present invention relates to a crystal growth apparatus destined for use in the growth of Group III(*a*) – V(*a*) compounds by solution epitaxy techniques.

2. Description of the Prior Art

Recently there has been a birth of interest in mixed crystals of gallium aluminum arsenide and gallium aluminum phosphide, it having been theorized that such crystals are capable of emitting light in the visible portion of the spectrum. Heretofore, workers in the art have succeeded in growing epitaxial films of gallium aluminum arsenide by dipping techniques. However, attempts to grow gallium aluminum phosphide in this manner have not proven fruitful. A later stage in the development of the art involved attempts by workers in the art to grow epitaxial films of gallium aluminum arsenide, and gallium aluminum phosphide by conventional tipping techniques. Unfortunately, the presence of a deleterious oxide scum on the surface of source solutions prevented uniform wetting and growth of the seed crystal, thereby precluding the use of this procedure.

SUMMARY OF THE INVENTION

In accordance with the present invention, an apparatus suitable for use in the growth of epitaxial films of Group III(*a*) – V(*a*) compounds is described. The use of this novel tipping apparatus results in the growth of epitaxial gallium aluminum arsenide, gallium aluminum phosphide, aluminum arsenide and aluminum phosphide. Solution growth of these compounds is effected in a tipping apparatus including a moveable substrate holder adapted with means for removing deleterious oxide contaminants from the surface of a source solution prior to growth. Operation of the well-known tipping technique in conjunction with the described apparatus results in the growth of the noted epitaxial films as well as the growth of *p-n* electroluminescent junctions capable of emitting red light at room temperature.

It will be understood by those skilled in the art that for the purposes of the present invention the Group III(*a*) – V(*a*) compounds of the Periodic Table of the Elements are those set forth in the Mendelyeev Periodic Table appearing on page B2 in the 45 Edition of the "Handbook of Chemistry and Physics," published by the Chemical Rubber Company.

BRIEF DESCRIPTION OF THE DRAWING

The invention will be more readily understood by reference to the following detailed description taken in conjunction with the accompanying drawing wherein:

FIG. 1 is a front elevational view of an apparatus employed in the practice of the invention;

FIG. 2 is a cross-sectional view of the crystal growth tube of FIG. 1; and

FIGS. 3A through 3D are cross-sectional views in successive stages of manufacture of a *p-n* junction device of the present invention.

DETAILED DESCRIPTION

With further reference now to FIG. 1, there is shown a typical crystal growth apparatus utilized in the practice of the present invention. Shown in the figure is a crystal growth tube 11 typically comprised of quartz having an inlet 12 and an outlet 13 for the introduction and removal of gases, respectively, and a boat assembly 14. Boat 14 has disposed therein a moveable substrate holder 15, a pair of wells 16 and 17 for containing source solutions, and means 18 for actuating holder 15. Holder 15 is also adapted with means 19 and 20 for removing surface oxides and associated contaminants from the surface

of source solutions contained in wells 16 and 17. Tube 11 is shown inserted in furnace 21, adapted with a viewing port 22, furnace 21 being positioned upon cradle 23, which permits tipping of the growth tube 11.

FIG. 2 is an enlarged view partly in section of tube 11, substrate holder 15 having contained therein a substrate member 24. Referring now to an exemplary technique employed herein, a suitable substrate material is obtained, typically from commercial sources. Thus, for example, the substrate may be gallium arsenide or gallium phosphide. The material so obtained is next lapped and cleaned in accordance with conventional techniques to yield smooth surfaces. A cross-sectional view of a typical substrate is shown in FIG. 3A (*n*-type for exemplary purposes).

Next, an apparatus similar to that shown in FIG. 1 including a quartz growth tube and a carbon boat is selected. Following, a source solution consisting of either gallium, aluminum and arsenic, or gallium, aluminum and phosphorus is prepared. This end is attained by adding known quantities of solid gallium arsenide or gallium phosphide (99.9999 percent purity) obtained from commercial sources to known amounts of aluminum (99.9999 percent purity) contained in a solution of gallium so as to result in solutions of the desired composition. For the purposes of the present invention, the amount of aluminum employed ranges from approximately 0.2 – 15 atomic percent in the gallium-aluminum-arsenic solutions, and approximately 0.2 – 4 atomic percent in gallium-aluminum-phosphorus solutions, the lower limits being dictated by considerations of the ternary phase diagram. The use of less than the noted amounts of aluminum is difficult because of the properties of the gallium-aluminum-arsenide phase system, whereas the use of greater than the noted amounts results in either aluminum arsenide or aluminum phosphide. An appropriate dopant may be added in order to obtain an epitaxial film of desired conductivity type. The components for the solution or solutions are placed together in the wells of the apparatus which are designed so that the upper surface of the solution is slightly above the edge of the well, the components being mixed and dissolved during subsequent heating. Then, the substrate member is inserted in the substrate holder and the system flushed with nitrogen. After flushing the system, pre-purified hydrogen is admitted thereto, and the temperature elevated to either 1,050° C. for gallium arsenide, or 1,150° C. for gallium phosphide, the temperature maximum being dictated by considerations relating to substrate damage and concomitant loss of arsenic or phosphorus. Following, the ram of the apparatus is activated by tipping the boat, thereby causing the leading edge of the substrate holder to remove the oxide scum from the surface of the solution contained in one of the wells and causing deposition of the substrate upon a clean oxide free solution. A controlled cooling program is then initiated at a rate sufficient to grow an epitaxial film of the desired thickness. The film 32, so grown, for example, of n-type conductivity may be seen by reference to FIG. 3B. At this point in the processing, a reverse tip may be effected so as to cause the substrate holder to shift in the opposite direction and deposit the substrate member on a clean oxide surface of a solution of differing concentration or containing a different dopant, thereby forming an epitaxial film 33 of, for example, *p*-type conductivity (FIG. 3C). In this manner, it is possible to form a *p-n* junction structure of the type noted above.

An example of the present invention is set forth below.

EXAMPLE

This example describes the fabrication of an electroluminescent p-n junction device utilizing gallium aluminum arsenide grown in accordance with the invention.

A gallium arsenide wafer having faces perpendicular to the <111> direction, obtained from commercial sources, was selected as the substrate member. The wafer was lapped with 305 "Carborundum," rinsed with deionized water, and etched for 30 seconds in a chlorine-methanol solution to remove sur-

face damage. Following, a gallium-aluminum-arsenic solution containing 0.8 atom percent aluminum, 9.2 percent arsenic, and 90 percent gallium, was prepared by adding 150 milligrams of gallium arsenide (99.9999 percent purity) obtained from commercial sources, and 50 milligrams of gallium arsenide doped to 10^{19} atom/cm^3 with tellurium to one gram of liquid gallium metal (99.9999 percent purity) containing four milligrams aluminum. The aluminum was prepared by cutting four milligrams of aluminum from a rod, etching it in sodium hydroxide and rinsing in deionized water. The tellurium in the tellurium doped gallium arsenide added to the solution was the source of tellurium to make the grown layer *n*-type. The components of the mixture were then placed in a well of the apparatus shown in FIG. 1. A second solution prepared in the manner described above was placed in the other well of the apparatus. However, this solution contained five milligrams of zinc, and instead of tellurium doped gallium arsenide all of the gallium arsenide used for the solution was undoped. The substrate member was then inserted in the substrate holder of the apparatus. The system was then sealed and nitrogen admitted thereto for the purpose of flushing out entrapped gases. Next, hydrogen was passed through the system and the temperature thereof elevated to approximately 1,040° C. After attaining this temperature, the oven was cooled to 1,000° C. and the ram in the apparatus was actuated by tipping the boat, thereby resulting in removal of the oxide scum from the surface of the solution containing the tellurium dopant, and the substrate member deposited thereon. At this point, a controlled cooling program at 2.5° C. per minute was initiated and the source solution cooled to approximately 990° C. over a time period of four minutes, thereby resulting in the formation of an epitaxial film of n-type gallium aluminum arsenide upon the gallium-arsenide substrate, such film having a thickness of approximately 0.87 mil. Then the apparatus was tipped in the other direction and the gallium-arsenide substrate bearing an *n*-type layer of gallium aluminum arsenide was again moved by actuating the ram of the apparatus and positioned upon the surface of the solution contained in the other well. The controlled cooling program was continued and a film of *p*-type gallium aluminum arsenide was grown upon the previously grown n-type gallium-aluminum-arsenide film over a temperature range of 990° – 970° C. during a time period of eight minutes. After attaining the desired *p-n* junction structure, the apparatus was tipped back to the horizontal and cooled to room temperature.

The resultant p-n structure was then diced to a geometry designed for device applications. Next, the bottom surface of the substrate was coated with 5,000 A. of titanium and 5,000 A. of gold by conventional evaporation techniques. Contact to the *n*-type material was made by depositing approximately 1×10^4 A. of tin thereon. The resultant structure is then mounted on a conventional transistor type header **34** (FIG. 3D) using low melting solder. The resultant structure may be seen in FIG. 3D in cross section. Ohmic contact is made to the *p*-side by means of tin film **35** and gold wire **36** and to the *n*-side by means of the titanium-gold film **37**.

In order to demonstrate the efficacy of the resultant devices, the leads were connected to a d-c source under forward bias conditions, the plus lead to the p-region and the minus lead to the n-region. At room temperature, at a forward voltage of +10 volts, the device was found to carry about ten milliamperes of current accompanied by the emission of red light. The measured external quantum efficiency as determined by means of a calibrated solar cell was found to be approximately 1×10^{-4} percent.

While the invention has been described in detail in the foregoing specification and the drawings similarly illustrate the same, the aforesaid is by way of illustration only and is not restrictive in character. The modifications which will readily suggest themselves to persons skilled in the art are all considered within the scope of this invention, reference being had to the appended claims. It will also be understood that the invention may be employed in the growth of epitaxial films which do not include aluminum.

We claim:

1. Crystal growth apparatus including:

a. a growth tube having disposed therein a boat assembly including:

1. at least one well located in the base thereof for containing a source solution;
2. an H-shaped substrate holder situated upon the base of the boat assembly, said holder including a three-sided chamber for containing a substrate member, the legs of said chamber being parallel to and equidistant from the vertical members of the H and perpendicular to and below the horizontal member of the H; and
3. actuating means adapted to slide between the vertical members of the H in response to movement of the growth tube whereupon the H moves so that the three-sided chamber passes over the well and is coextensive therewith;

b. means for tipping said growth tube from a first direction to a second direction, thereby effecting movement of said actuating means and said substrate holder.

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