United States Patent

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[54] HORIZONTAL LIQUID PHASE EPITAXY APPARATUS

5 Claims, 6 Drawing Figs.

[52] U.S. Cl. 118/421, 118/500
[51] Int. Cl. B05c 3/00
[50] Field of Search 118/421, 500, 506

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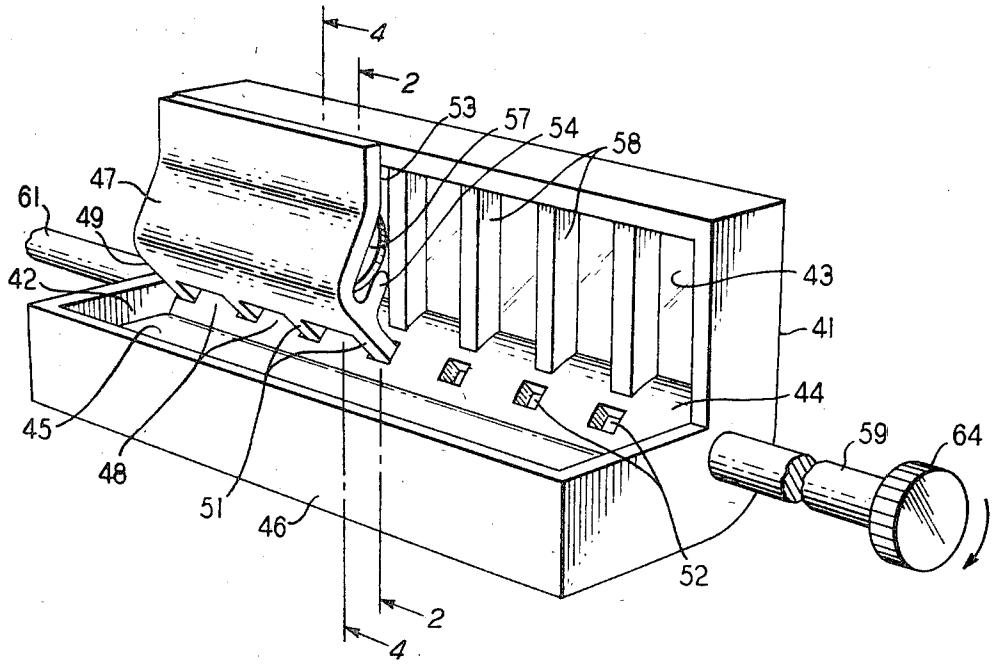
ABSTRACT: A liquid phase crystal growth apparatus designed to permit simultaneous growth upon a plurality of substrates is described. The apparatus includes a container having a pair of compartments for containing a melt during various stages in the operation of the process, one of said compartments including means for holding the substrates. In the growth process, the container is rotated, thereby effectuating flow of the melt from one compartment to the other with the concurrent dropping of substrates upon the melt surface. Growth is then initiated by cooling a saturated melt.



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SHEET 1 OF 2

FIG. 1

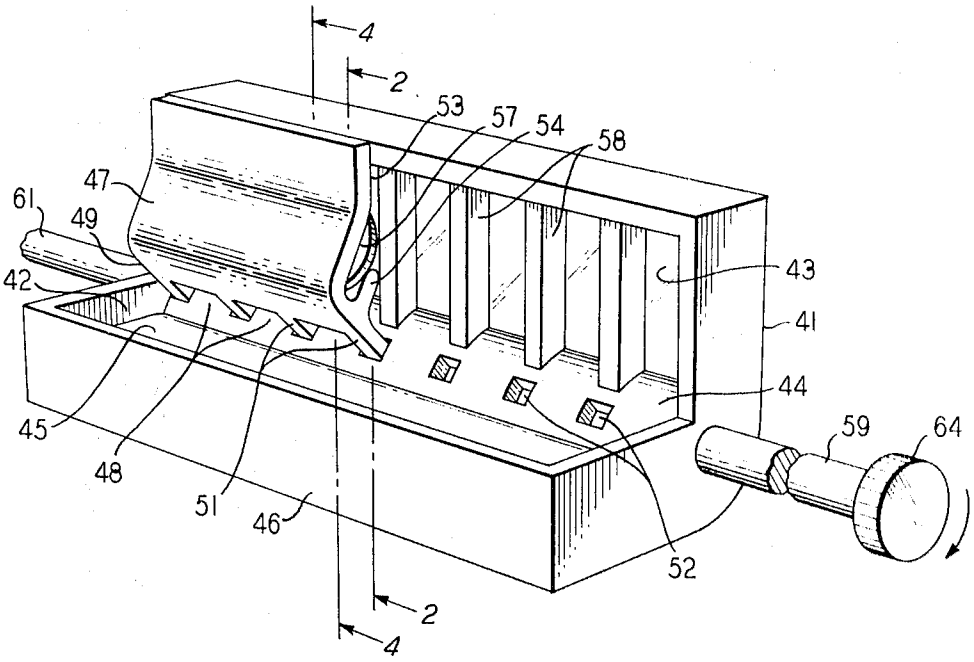

FIG. 2

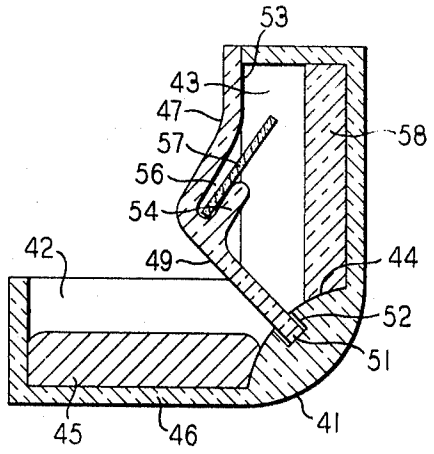

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FIG. 3

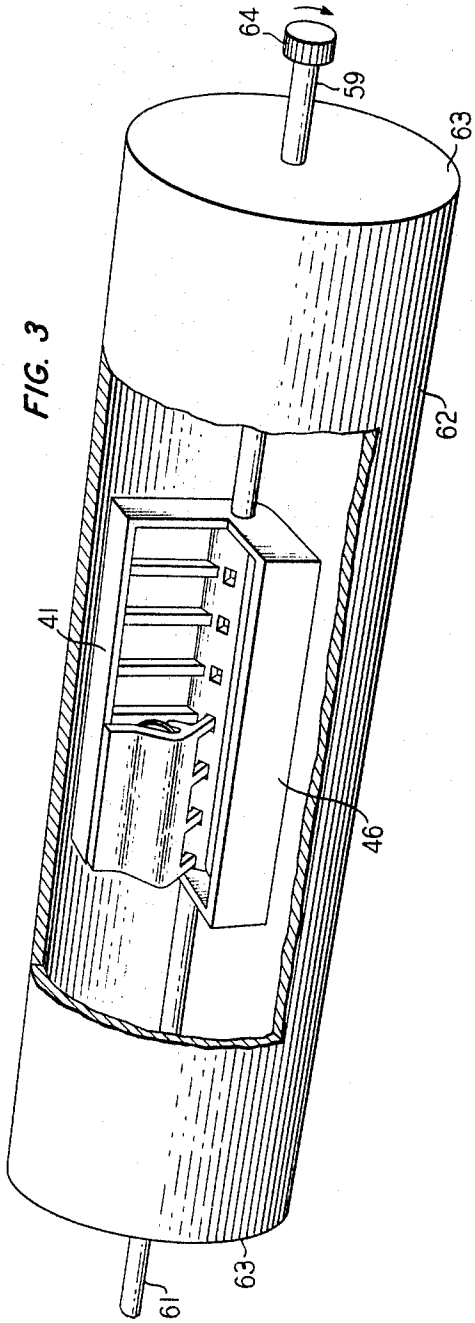


FIG. 4C

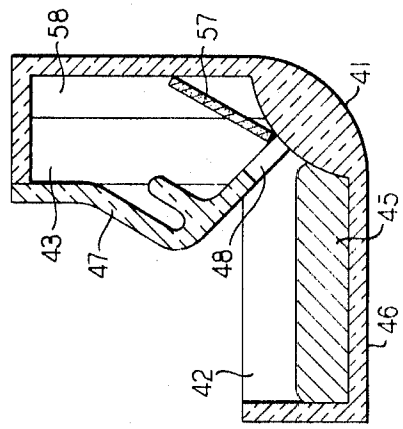


FIG. 4B

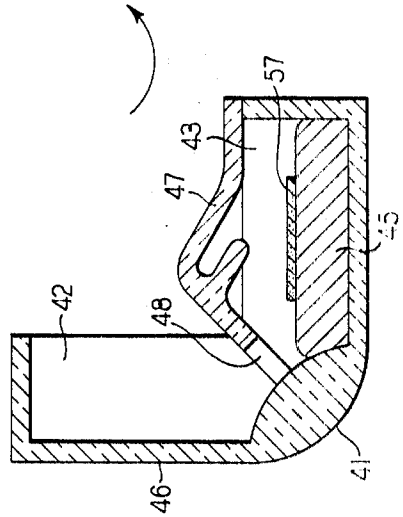
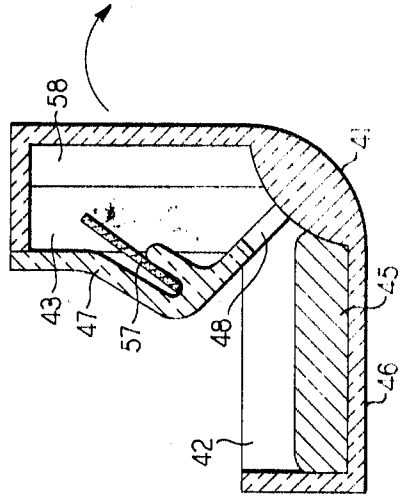


FIG. 4A



HORIZONTAL LIQUID PHASE EPITAXY APPARATUS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a liquid phase crystal growth apparatus, and more particularly to a horizontal apparatus for simultaneous liquid phase crystal growth upon a plurality of substrates.

2. Description of the Prior Art

Heretofore, crystal growth, especially epitaxial growth, from the liquid phase has often been done with a horizontal tipping apparatus. In a typical example of such a technique, a GaAs substrate wafer is held tightly against the upper end of a graphite boat and a tin-GaAs mixture is placed at the lower end. The graphite boat is then fixed at the center of a constant-temperature zone, within a quartz furnace tube which is tipped in one direction. The furnace tube is heated so that the GaAs dissolves in the tin at the lower end of the boat. At this point, the furnace tube is tipped in a second direction to allow the molten tin to run over the exposed surfaces of the GaAs substrate. The furnace tube is cooled and the GaAs precipitates from the melt and epitaxial growth of the GaAs on the substrate occurs. This growth is allowed to continue for a prescribed interval to yield the desired growth thickness. However, it is to be understood that as the furnace tube is cooled, the top surface of the melt has a lower temperature which results in precipitation at that surface. This leads to certain uncontrolled amount of growth on the substrate. The melt is then decanted from the surface of the substrate by tipping the tube back to its original position so that the excess melt flows off.

Since the apparatus is tipped out of a horizontal plane in order to have the melt flow upon the substrate surface, the substrate is maintained in a plane which deviates from a horizontal plane, thus causing the melt to cover the substrate across its surface to a depth which is nonuniform. This nonuniformity therefore leads to a nonuniformity in the rate of cooling which in turn results in a horizontal temperature gradient across the substrate surface. Unfortunately, this gradient may result in (1) an irregular thickness of the regrown surface, (2) a variable doping profile over the regrown layer, and (3) a damaged interface between the substrate and the regrown layer. It is also to be understood that such a tipping apparatus can accommodate only one substrate at a time. An apparatus in which simultaneous horizontal liquid phase crystal growth upon a plurality of substrates could be effected and which would permit uniform depth coverage across the substrate surface by the melt has long been sought.

SUMMARY OF THE INVENTION

The present invention is directed to a horizontal liquid phase crystal growth apparatus. The apparatus consists of a container or boat which can be rotatably mounted within a suitable furnace. The container comprises a first compartment for holding a melt when the base of the container is in a first direction and a second compartment for holding the same melt when the base is in a second direction. Disposed within the second compartment and attached thereto is a substrate holder for holding a plurality of suitable substrates when the base of the container is in the first direction. The first compartment is connected with the second by a plurality of conduits which channel the melt between the compartments. Attached to the container is a means for rotating the base from the first to the second direction.

In operation, suitable substrates are placed in the substrate holder. A melt mixture containing the material to be grown and a solvent metal is placed in the first compartment and the container is heated in order to form a saturated solution. Upon reaching the desired temperature, the container is rotated leading to the following series of sequentially occurring steps:

1. the base rotates from the first direction into the second direction,

2. the melt flows from the first compartment through the conduits into the second compartment, and

3. the substrates are deposited atop of the melt. Crystal growth is then allowed to proceed under standard growth conditions, i.e., by cooling the furnace. The growth is then terminated by rotating the container back to its original position.

DESCRIPTION OF THE DRAWING

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

FIG. 1 is a cutaway perspective view of the horizontal liquid phase crystal growth apparatus of the invention;

FIG. 2 is a cross-sectional view of the apparatus taken along line 2–2 of FIG. 1;

FIG. 3 is a perspective view of the liquid phase crystal growth apparatus of FIG. 1 mounted within a typical furnace;

FIG. 4A is a cross-sectional view of the apparatus, taken along line 4–4 of FIG. 1 prior to rotation of the apparatus;

FIG. 4B is a cross-sectional view of the apparatus, taken along line 4–4 of FIG. 1 after rotation of the apparatus clockwise 90°; and

FIG. 4C is a cross-sectional view of the apparatus, taken along line 4–4 of FIG. 1, after rotation of the apparatus counterclockwise 90°.

DETAILED DESCRIPTION

The present invention has been described only in terms of the epitaxial growth of GaAs and GaP on substrates of GaAs and GaP, respectively. However, it will be understood that such description is for purposes of exposition and not for purposes of limitation. It will be readily appreciated that the inventive concept described is equally applicable to nonepitaxial as well as epitaxial growth and to crystal growth of nonsemiconductor materials as well as semiconductor materials. Also the inventive concept described is applicable to many combinations of substrate and melt whereby both homojunctions and heterojunctions are formed. Regarding the epitaxial growth of semiconductor materials, the materials may be selected from among group III—V compounds, group II—VI compounds, or group IV elements of the Periodic Table of the Elements as set forth in the Mendelyeev Periodic Table appearing on page B2 in the 45th edition of the "Handbook of Chemistry and Physics," published by the Chemical Rubber Company.

With reference now to FIG. 1, there is shown the crystal growth apparatus utilized in the practice of the present invention. Shown in the figure is an L-shaped container or boat **41**, which can be fabricated from any inert material including such materials as high-purity graphite, alumina, quartz, boron nitride, or any inert ceramic material. It is to be understood that all the above-mentioned materials, including graphite, may or may not be employed with a high-purity graphite liner.

The container **41** is divided into two compartments **42** and **43** by means of a longitudinally extending ridge **44**. The first compartment **42** is destined for holding a melt **45**, composed of a solvent metal, semiconductor and dopants, when the base **46** of the container **41** lies in a first direction, which for purposes of illustration only is along a horizontal plane. The second compartment **43** is destined for holding the same melt when the base **46** lies in a second direction which deviates from the first direction, i.e., out of a horizontal plane.

An angular plate **47**, constructed of the above-mentioned inert materials, covers compartment **43**. This plate **47** serves as a heat shield for compartment **43**, thereby approximating a perfect block body and insuring a uniform cooling or heat dissipation during the crystal growth operation. A series of conduit passageways **48** are cut out of the lower wall **49** of plate **47**, defining wall posts or columns **51**. Plate **47** is affixed to container **41**, thereby covering compartment **43** and serving as a heat shield, by means of these posts **51** which fit into locating holes **52** formed in ridge **44**. When plate **47** is thus affixed, the conduit passageways **48** connect compartment **42**

with compartment 43 and are destined for channeling the melt between the compartments. Extending across the interior surface 53 of plate 47 is a lip 54. Referring to FIG. 2, the top surface of the lip 54 and the interior surface 53 define a slot 56 which is designed to hold a plurality of substrates 57 when the base 46 lies in the first direction.

Referring again to FIG. 1, within compartment 43 are a plurality of ribs or partitions 58 which are situated in tin-GaAs relation to conduit openings 48, the function of such partitions being to permit the formation of individual pools of melt for each substrate upon which growth is to be affected during the operation of the process. Ribs 58 are spaced so as to permit individual substrates such as 57, to be accommodated when lying flat and also to prevent the substrate wafers 57 from a possible intermingling when in contact with the melt during crystal growth. It is to be understood however that the apparatus is operable with or without such partitions 58 and is not to be restricted thereby.

Attached to both ends of container 41 are two rods 59 and 61, fabricated from the above-mentioned inert materials, which are in alignment with one another. Referring to FIG. 3, the rods 59 and 61 are used to insert and support the container in a typical furnace 62. The rods 59 and 61 fit into and are supported by end plates 63 of the furnace 62. Attached to rod 59 is a handle 64 which is used to rotate the container 41 and thus rotate the base 46 as desired. In this regard, it is to be noted that the rotation and support of container 41 is not limited to the use of rods and any standard means can be employed, such as for example, a carriage arrangement which can rotate either the container 41 individually or the furnace 62 and container 41 collectively.

Referring now to an exemplary technique, a suitable *n*-type gallium arsenide substrate material is obtained, typically from commercial sources. The material so obtained is cut into a plurality of wafers which are then lapped and cleaned in accordance with conventional techniques to yield smooth surfaces. Next, an apparatus constructed from high-purity graphite, similar to that shown in FIG. 1, is selected. A plurality of cleaned and lapped gallium arsenide wafers or substrates 57 is inserted into slot 56 of plate 47. The plate 47 is then affixed to container 41 whose base 46 lies in a horizontal plane, by inserting posts 51 into locating holes 52.

A Tin-GaAs mixture is prepared by first cutting *n*-type GaAs, obtained from commercial sources, to a size to fit into compartment 42. Following, tin of 99.9999 percent purity, obtained from commercial sources, is weighed out in a precleaned graphite boat and placed in compartment 42 of container 41. The gallium arsenide is then weighed out, in an amount sufficient to result in a gallium arsenide saturated tin solution, whereupon it is added to the weighed out tin contained in compartment 42. Typically the composition meeting the saturation requirement is in the range of 6 to 10 mole percent GaAs.

Referring to FIG. 3, the container 41 is then placed in a suitable horizontal furnace 62, such as a standard diffusion furnace, wherein the container 41 is supported by means of rods 59 and 62, base 46 lying in a horizontal plane, (first direction). The container 41 is then fixed in position at the center of a constant temperature zone of furnace 62; and, subsequently, furnace 62 is flushed with nitrogen admitted to the system through suitable inlet and outlet means (not shown). After flushing with nitrogen, hydrogen is allowed to flow into furnace 62 and container 41 is heated to Ca 600° C. thereby causing the GaAs particles to dissolve in the tin, thereby resulting in a saturated GaAs melt.

When the temperature reaches 600° C., the heating power is reduced to maintain the temperature at or slightly below 600° C., and container 41 is rotated clockwise by handle 63. As indicated in FIG. 1 and FIGS. 4A and 4B, rotating the container initiates the following series of sequentially occurring steps:

1. base 46 rotates from the first direction, i.e., a direction parallel to the horizontal plane, to the second direction which deviates from the horizontal plane;

2. melt 45, initially contained in compartment 42, passes from compartment 42 through conduit 48, into compartment 43 wherein it forms pools defined by ribs 58; and

3. the GaAs substrates 57 are no longer held in slot 56 and are deposited atop the individual pools of melt 45, being prevented from intermingling by ribs 58 which separate each individual substrate. Regarding step (1) above, it is to be noted in reference to FIGS. 4A and 4B that base 46 has been rotated 90° out of the horizontal plane into a vertical plane. It will be appreciated that such is for illustrative purposes only, and container 41 can be so designed as to initiate the above sequence of steps with almost any degree of rotation.

After substrates 57 have been deposited upon the melt, the furnace is cooled at a constant cooling rate of approximately 12° per minute, by means of a controlled cooling program, until a temperature of approximately 500° C. is attained. During the cooling cycle, precipitation of GaAs from the solution is initiated, thus resulting in the growth of an *n*-type GaAs epitaxial film upon the substrates 57. In this regard, it is to be understood that plate 47 has been so designed as to insure uniform heat dissipation from compartment 43, thereby improving the uniformity of crystal growth.

When the temperature of container 41 reaches 500° C. the cooling of the furnace is halted. The crystal growth is terminated by rotating container 41 counterclockwise 90°, as illustrated in FIG. 4C, thus causing the following series of sequentially occurring steps:

1. base 46 rotates from the second direction to the first direction,

2. melt 45 contained in compartment 43 flows from said compartment through conduit 48 back into compartment 42, and

3. the substrates 57 are left resting in compartment 43.

In another exemplary embodiment, a suitable *n*-type tellurium doped GaP substrate material, grown by standard liquid encapsulated pulling technique, is cut into a plurality of wafers which are then lapped and cleaned in accordance with conventional techniques. A plurality of cleaned and lapped *n*-type GaP wafers or substrates 57 so obtained are inserted and affixed to an apparatus fabricated from graphite, similar to that shown in FIG. 1, by the technique previously described. A gallium-high resistivity GaP-Ga_2O_3-Z_n mixture is prepared by first weighing out high-purity gallium, Z_n and Ga_2O_3, obtained from commercial sources, and inserting the above components into compartment 42. The high resistivity gallium phosphide is cut to fit into compartment 42, weighed out, and then added to the gallium, Z_n and Ga_2O_3, in compartment 42. The amount of GaP employed is such as to form a saturated gallium solution at the desired temperature. Typically, the composition meeting the saturation requirement is in the range of 0.2 to 12 mole percent GaP, in the temperature range of 800°—1,200° C.

The container 41 is again placed in a suitable furnace 62 and fixed in position, as previously described, so that the base 46 lies in the horizontal plane (first direction). The system is flushed with nitrogen and then hydrogen is admitted whereupon the container 41 is heated to a temperature in the range of 1,050°—1,060° C., so resulting in the formation of a saturated GaP—gallium metal doped with Z_n and oxygen. When the temperature is in the range of 1,050°—1,060° C., further heating is discontinued and container 41 is rotated clockwise in the manner previously described, which initiates the following series of sequentially occurring steps:

1. base 46 rotates from the first direction to the second direction,

2. melt 45 passes from compartment 42 through conduit 48 into compartment 43 wherein the melt 45 forms pools defined by ribs 58, and

3. the GaP substrates 57 are deposited atop the individual pools of melt 45.

After the GaP substrates 57 have been deposited upon the melt, the furnace is cooled at a rate of 2°—5° per minute until the temperature of the container 41 has dropped 20° to 50° C. whereupon the container is rotated counterclockwise as previ-

ously described. Typically, the GaP substrates are in contact with the melt from 4 to 50 minutes leading to a grown crystal layer of from ½ to 3 mils.

What I claim is:

1. A liquid phase crystal growth apparatus which comprises:
a. a container;
b. a first compartment within said container for holding a melt when the base of said container lies in a first direction;
c. a second compartment within said container for holding said melt when the base lies in a second direction;
d. an open-top, slot-type, substrate holding means disposed within an upper portion of said second compartment for loosely holding at least one substrate when the base lies in said first direction;
e. rotating means attached to said container for rotating the base from said first direction into said second direction and back into said first direction;
f. a conduit means for channeling said melt from said first compartment to said second compartment when said base rotates from said first direction to said second direction; and
g. said substrate holding means, compartments and conduit means being structurally so related whereby, upon rotation of the containers from the first direction to the second direction, said substrate is released from the holding means and deposited upon said melt in the second compartment.

2. The apparatus as defined in claim 1 which further comprises a heat dissipation means covering said second compartment for uniformly dissipating heat from said second compartment.

3. The apparatus as defined in claim 2 wherein said heat-dissipating means is a heat shield.

4. The apparatus as defined in claim 1 wherein a plurality of said substrate-holding means are disposed within said second compartment and said second compartment comprises a separate melt holding portion associated with the separate ones of said plurality of substrate holding means.

5. The apparatus as defined in claim 4 wherein means are disposed to retain said substrates within the second compartment when the container is rotated back from said second direction to the first direction while permitting the nonconsumed melt to be returned to said first compartment.