

[54] VERTICAL LIQUID PHASE CRYSTAL GROWTH APPARATUS

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[51] Int. Cl. B05c 3/18

[58] Field of Search 118/400, 429, 415; 148/172, 148/173, 174

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[57] ABSTRACT

A vertical liquid phase crystal growth apparatus includes (1) a container for housing a melt and either a single substrate or a plurality of substrates, (2) a furnace, and (3) a heat sink. The melt and the substrates are isolated from one another prior to the growth process by means of a cover plate which restricts the free volume surrounding the substrate(s). The container is heated to the desired temperature and the saturated melt containing the desired dopants and the substrate are allowed to come into contact by lifting the plate. Growth is then initiated from a convection-free melt by cooling the container and, thus, the substrate by means of a heat sink which establishes a thermal gradient along the vertical axis of the container.

5 Claims, 4 Drawing Figures

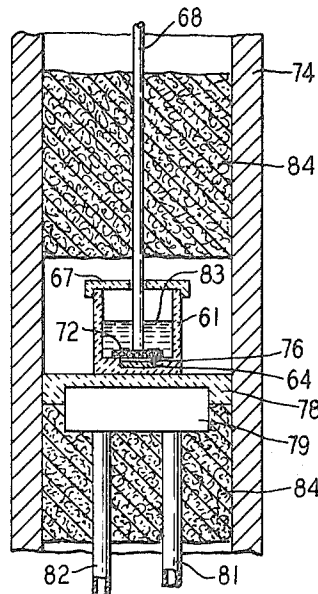
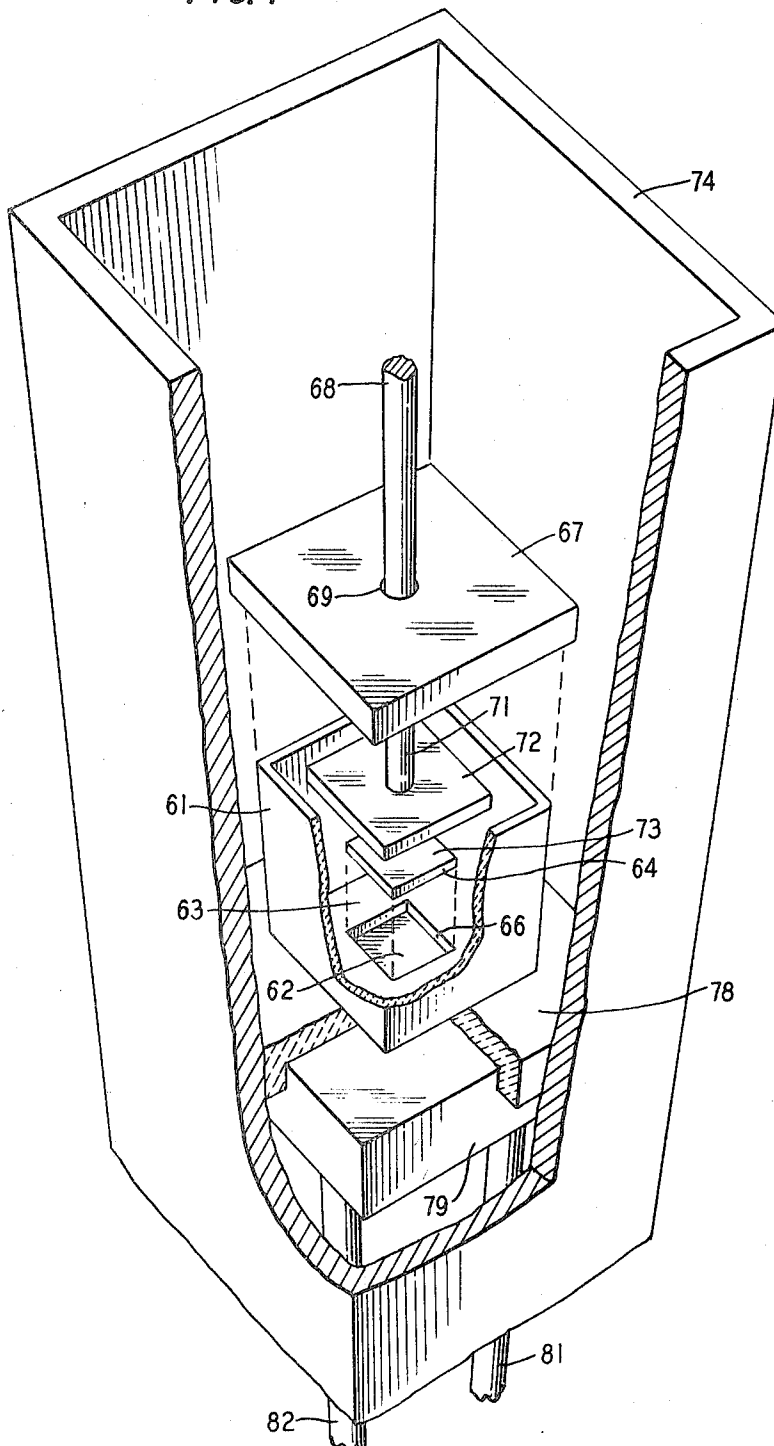


FIG. 1



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FIG. 2

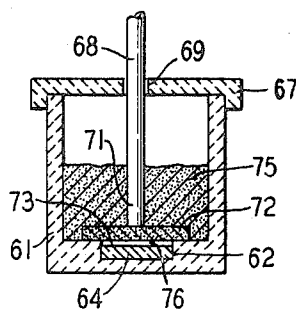


FIG. 3

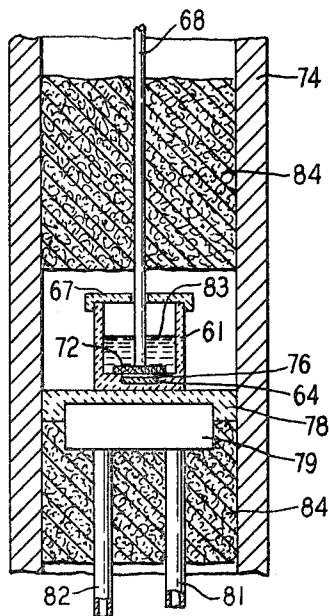
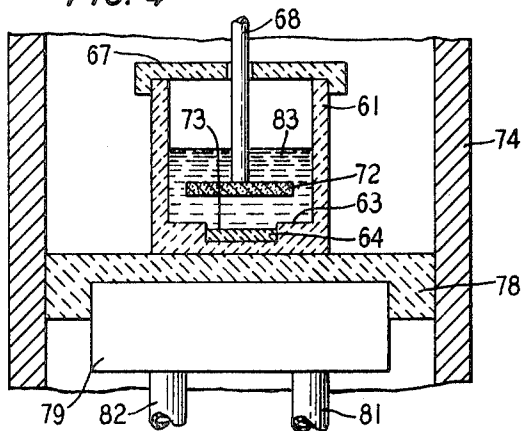


FIG. 4



VERTICAL LIQUID PHASE CRYSTAL GROWTH APPARATUS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a vertical liquid phase crystal growth apparatus and more particularly, to a vertical apparatus which incorporates a heat sink means to establish a vertical temperature gradient during growth.

2. Description of the Prior Art

Heretofore, crystal growth from the liquid phase has been accomplished with a multiplicity of vertical liquid phase apparatus. However, the quality of the regrown layers, especially in epitaxial growth has been adversely affected by the quality of the substrate material as well as by temperature gradients in the melt. Surface degradation of the substrate most often occurs from (1) decomposition of the substrate followed by volatilization of an element therefrom at elevated temperatures, (2) the transfer of volatile compounds from the melt to the substrate and (3) the transfer of foreign particles to the substrate surface from the melt.

An apparatus which restricts the free volume surrounding the substrate and which physically separates the substrate from the melt would alleviate the first two above-mentioned causes of surface degradation. Since most impurities have a lower density than the usual melts employed in liquid phase growth, small particles of contamination usually float atop the melt. Apparatus has been developed heretofore in which the melt is "skimmed" prior to contacting the substrate; however, the clean surface required entails extreme care, and it would be much easier and safer to construct an apparatus which prevents the substrate from contacting the liquid-gas interface, thereby eliminating the third above-mentioned cause of surface degradation.

In addition to the above-noted difficulties, convective currents in the melt during regrowth 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. If cooling starts at the top of the melt or if regrowth is initiated at the top, gravity causes the heavier solution to sink and form convective cells. To avoid convection, a vertical temperature gradient must be established with a decreasing temperature toward the lowest part of the system. However, the apparatus should have a horizontal temperature gradient of zero in order to obtain a uniform thickness of the regrown layer.

SUMMARY OF THE INVENTION

The present invention is directed to a vertical liquid phase crystal growth apparatus, which optimizes the growth by (1) maintaining the free volume surrounding the substrate at a minimum, (2) physically segregating the substrate from the melt prior to growth, (3) preventing melt-substrate contact at the liquid-gas interface and (4) providing a vertical thermal gradient with isothermal conditions in the horizontal direction whereby the substrate is maintained at the lowest temperature.

The vertical apparatus consists of a container for housing a melt and a substrate. The base of the container has a compartment or well which intimately accommodates the sides of the substrate. Isolating the substrate from the melt when the container is maintained at an initial or first temperature is a cover plate which covers the substrate. Attached to the cover plate is a rod which raises the cover plate from the substrate when the container is maintained at a second temperature, thereby leading to contact between the substrate and the melt. Covering the container is a lid which insures uniform heat dissipation from the container and through which the rod slideably passes. Contacting the base of the container is a heat sink which insures a vertical temperature gradient during growth.

In operation, a suitable substrate is placed in the container within the well. The cover plate is placed over the substrate and a melt mixture containing the material to be grown and

the required dopants is placed in the container atop and surrounding the cover plate. The lid is affixed in place and the container is heated to a first temperature to form a solution from the melt mixture. Upon reaching a second temperature, the cover plate is raised so as to uncover the substrate and allow the saturated melt to come in contact with and cover the substrate. Crystal growth is then allowed to proceed by cooling the substrate, employing a heat sink means. A vertical temperature gradient is provided to insure deposition from a convection-free melt.

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 perspective view of the vertical liquid phase crystal growth apparatus of the invention;

FIG. 2 is a cross-sectional view of the growth container after being loaded with the substrate and the melt mixture;

FIG. 3 is a cross-sectional view of the loaded container contained within the vertical furnace; and

FIG. 4 is a cross-sectional view of the apparatus during crystal growth.

DETAILED DESCRIPTION

The present invention has been described largely in terms of the epitaxial growth of P-type GaP on a substrate of P-type GaP. 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 homojunctions and heterojunctions are formed. Regarding the epitaxial growth of semiconductor materials, the materials may be selected from among group III(a)-V(a) compounds, group II(b)-VI(a) compounds or group IV elements of the Periodic Table of the Elements as set forth in the Mendelyev 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 vertical crystal growth apparatus of the present invention. Shown in the figure is a container or boat 61, 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 of the above-mentioned materials, including graphite, may or may not be employed with a high purity graphite liner (not shown). It is also to be understood that although the container or boat 61 has been shown to be rectangular in shape, the inventive concept need not be restricted thereby and the container may be parallelepiped or cylindrical in shape.

The container 61 has a compartment or well 62, on its base 63, destined for accommodating a substrate 64 flush against the walls 66 of the compartment 62. Covering the container 61 is a lid 67 which is constructed of the above-mentioned inert materials and which serves to insure uniform heat dissipation from the container 61.

A rod 68 made of the above-mentioned inert materials slideably passes through an aperture 69 in the lid 67. Attached on one end 71 of the rod 68 is a cover plate 72 which may be made of any of the above-mentioned materials. Preferably, the cover plate 72 should be constructed of the substrate material, e.g., GaP, to decrease the surface degradation of the substrate via loss of any volatile elements therefrom and to assure a saturated melt. It is to be noted at this point, that when the substrate 64 has been inserted into container 61, the top surface 73 of the substrate 64 is almost flush with the top surface of the base 63. Therefore, when the cover plate 72 covers the substrate 64 (FIG. 2) the free volume 76 surrounding the sub-

strate 64 is thereby maintained at a minimum. This minimization decreases the elemental loss due to evaporation from the substrate. The free volume maintained should ideally be one which limits the loss due to evaporation to one monolayer of the surface of the substrate. The free volume is therefore dependent upon the substrate employed and the vapor pressures involved.

The container 61 is contained within a vertical furnace 74, supported therein by a pedestal 78. Incorporated within the furnace 74, as shown in FIGS. 1 and 3, is a heat exchanger 79, wherein gas maintained at low temperatures is introduced via inlet 81 through the heat exchanger 79 and out through outlet 82. In this regard, it is to be noted that the heat exchanger has been described in terms of a cooling gas exchanger, but the inventive embodiment is not to be restricted thereby and any heat sink means may be employed.

Although the invention has been described for illustrative purposes in terms of one substrate and one compartment for retaining said substrate, it will be understood that the apparatus may include a plurality of substrates accommodated within a plurality of compartments, all of which are within a single container and covered by either one large cover plate or a plurality of cover plates.

Referring now to an exemplary technique, a suitable P-type GaP substrate material grown by standard liquid encapsulated pulling techniques is cut to size whereupon it is lapped and cleaned in accordance with conventional techniques. Referring to FIGS. 1 and 2, the lapped and cleaned GaP substrate 64 is inserted into a high purity graphite container 61 similar to that described in FIG. 1. This loading is accomplished in an inert ambient such as nitrogen. The substrate 64 is placed into well 62 and is thereupon covered by a cover plate 72 which is fabricated of GaP and to which is attached a high purity graphite rod 68.

A gallium—GaP—Ga₂O₃—Zn melt mixture 75 is prepared by first weighing out high purity gallium, Zn and Ga₂O₃ obtained from commercial sources. The high resistivity GaP material is cut and weighed out and then added to the gallium, Zn and Ga₂O₃ previously weighed out and the mixture 75 is added to the container 61 atop of the cover plate 72. 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.

After the melt mixture 75 has been inserted into the container 61, a high purity graphite lid 67 is placed over the container 61, rod 68 passing through aperture 69 of the lid 67. The lid 67 covers container 61 and insures uniform heat dissipation therefrom. Referring to FIG. 3, the container 61 is then placed within a standard vertical furnace 74 upon pedestal 78. Thermal insulation 84 is packed around the pedestal 78 thereby creating an isothermal center portion which accommodates the container 61.

The furnace 74 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 the furnace 74 and the container 61 is heated to a first temperature above the melting point of gallium thereby resulting in the formation of a melt 83. At this point, it should be noted that the substrate 64 is isolated or segregated from the melt 83 by means of the GaP cover plate 72 which prevents the transfer of volatile compounds to the substrate 64 prior to

deposition. Also, the free volume 76 surrounding the substrate 64 is maintained ideally at 0.01 mm. to restrict the loss due to volatilization to approximately one monolayer of the surface of the GaP substrate 64.

The container 61 is heated to a second temperature in the range of 1,050–1,060° C., resulting in the formation of a saturated P-type GaP gallium melt 83 doped with zinc and oxygen. Referring to FIG. 4, after thermal equilibrium is established between the substrate 64 and the melt 83, the cover plate 72 is lifted by raising rod 68 which results in the covering of the substrate 64 by the saturated melt 83. Due to the isothermal conditions, neither deposition on the substrate nor dissolution of the substrate occurs at this time. Also, the substrate is prevented from surface contamination via contact with the gas-melt interface.

A cooled inert gas such as nitrogen is flowed into inlet 81, through heat exchanger 79 and out through outlet 82. This causes the temperature of the pedestal 78, the base 63 and the substrate 64 contained within the container 61 to be lowered. A temperature gradient is established along the vertical axis of the container 61, the base 63 and the substrate 64 wherein the base 63 and the substrate 64 are at the lowest temperature. Crystal growth is thus initiated through the cooling of the saturated melt 83.

The growth process is terminated by lowering the cover plate 72 over the substrate 64. In the alternative, the furnace 74 can be tilted, thereby tipping off the melt 83 from the substrate 64. Typically, the GaP substrate 64 is in contact with the melt 83 from 4 to 50 minutes leading to a grown crystal layer of from ½ to 3 mils.

What is claimed is:

1. A vertical liquid phase epitaxial growth apparatus, which comprises:

- a container for housing a melt and a substrate;
- a compartment within the base of said container for holding said substrate;
- means for heating said container;
- cover plate means closing off said compartment for isolating said substrate from said melt when said container is maintained at a first temperature, said cover means comprising a portion of the bottom support for said melt;
- means adapted to raise said cover means whereby said cover is removed from its isolating position and said substrate is contacted by the melt when the container is maintained at a second temperature; and
- heat sink means contacting the base of said container for establishing a vertical temperature gradient along the vertical axis of said container.

2. The apparatus as defined in claim 1 wherein:

said compartment is adapted to intimately accommodate the sides of said substrate.

3. The apparatus as defined in claim 1 wherein said heating means is a vertical furnace.

4. The apparatus as defined in claim 1 which further comprises

a lid for covering said container for insuring a uniform heat dissipation from said container and wherein said raising means comprises a rod attached to said cover plate and slideably fitted through said lid.

5. The apparatus as defined in claim 3 wherein said heat sink is a heat exchanger maintained within said vertical furnace.

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