United States Patent [19]

Grandia et al.

[11] **3,881,037**

[45] **Apr. 29, 1975**

[54] **ISOTHERMAL SOLUTION MIXING GROWTH OF SOLIDS**

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[22] Filed: **May 15, 1973**

[21] Appl. No.: **360,518**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 84,523, Aug. 17, 1971, abandoned.

[52] **U.S. Cl.** ..... **427/87**; 148/171; 148/1.5; 148/172; 23/301 SP; 357/16

[51] **Int. Cl.** **H01l 7/00**; H01l 7/40

[58] **Field of Search** ..... 148/171, 172, 1.5, 1.6; 117/200, 201, 113; 23/301 SP

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[57] **ABSTRACT**

It has been discovered for the practice of this invention that when two melts at the same temperature which were separately and simultaneously saturated are mixed, the combined melt is supersaturated and crystal growth occurs isothermally. Mixing of different melts is caused to occur so as to control both composition and amount of growth of the resultant solid substance. A new technique for heterojunction growth has been discovered for the practice of this invention. The method has the capability for growing multilayered structures over a wide range of thicknesses and especially for layer thicknesses substantially less than 1 micron.

Generally, the practice of this invention provides solutions to several problems associated with the liquid phase epitaxy method. Specifically, it provides for the maintenance of GaAs surface in suitable form for high quality growth of a layer thereon and for the facility of controllably changing the layer composition in the case of semiconductor materials with more than two components.

Important features of the invention are: a partitioned crucible of isolating two or more melts; a window in each melt compartment which exposes the melt to the substrate when correctly aligned; and a substrate holder which can be positioned to allow contact with one melt and then repositioned to allow contact with one or more other melts without the loss of a solid-liquid interface. In the preferred embodiment of the invention, the windows are opened on the walls of an inner crucible; the substrate is held in two slots on a ground face of a cylindrical rod which can be rotated from one window to the next.

24 Claims, 13 Drawing Figures

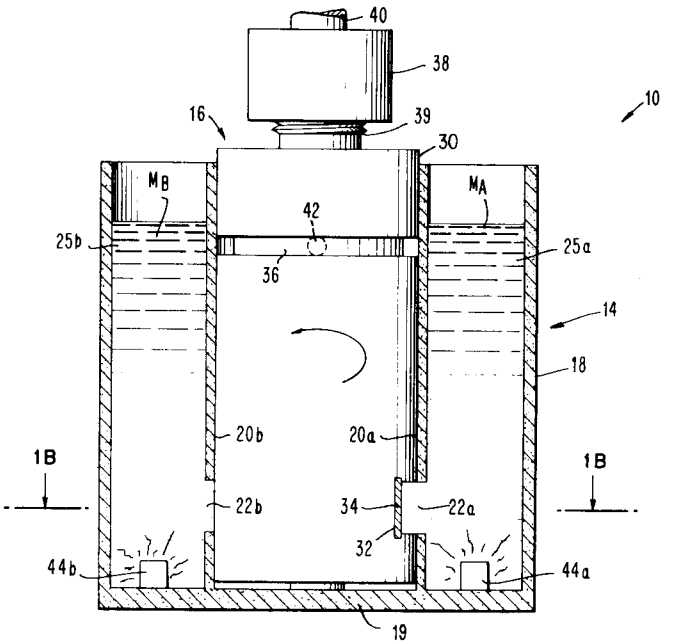


FIG. 1A

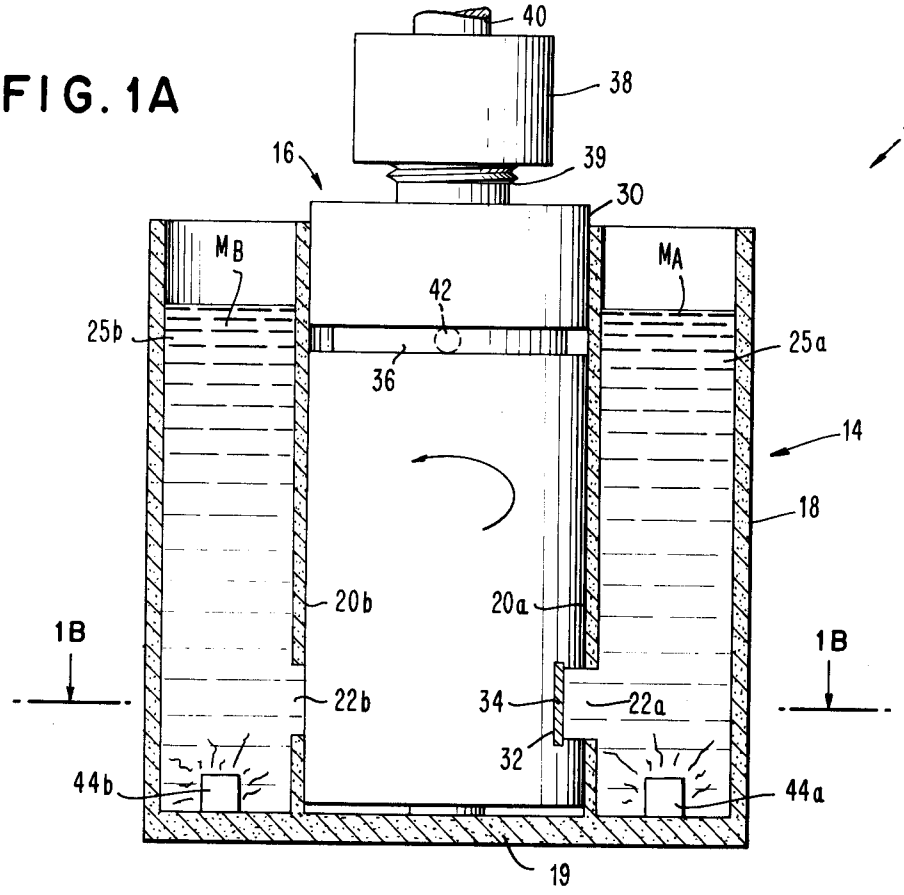
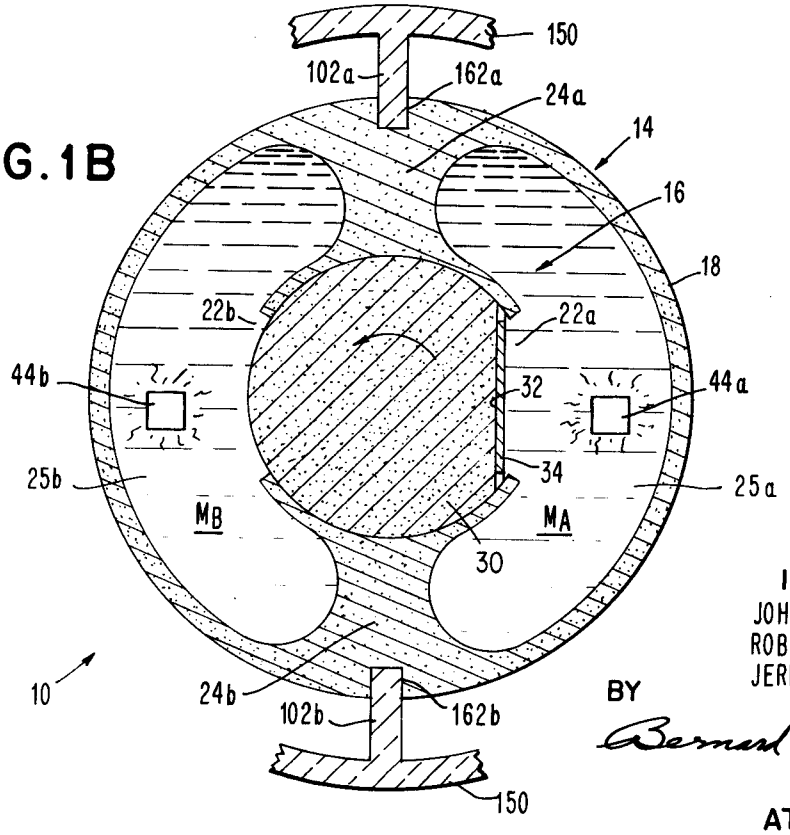


FIG. 1B



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FIG. 1C

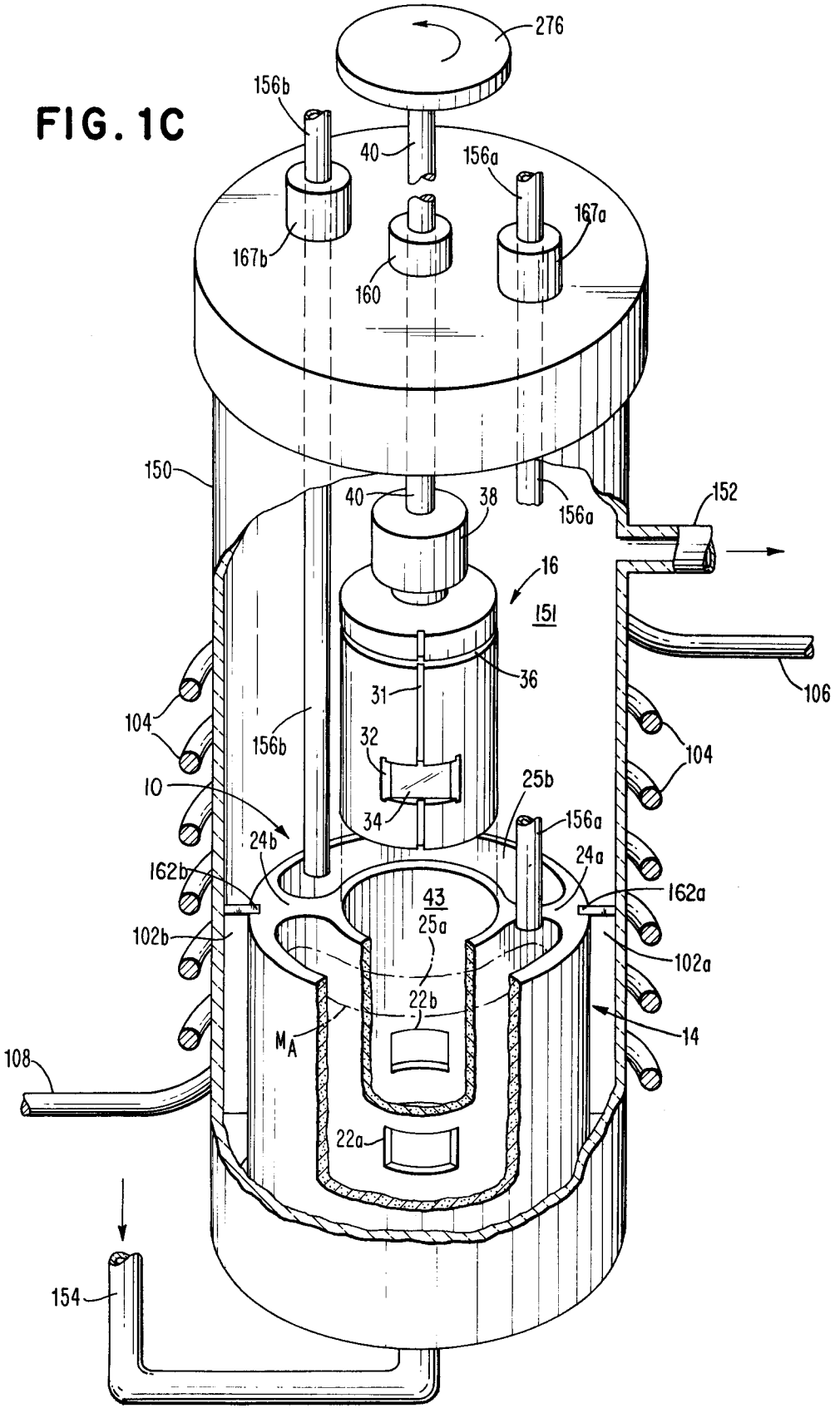

276
156b
40
156a
167a
167b
160
150
40
38
156a
152
16
151
36
106
31
104
156b
32
104
10
25b
34
156a
24b
24a
162b
162a
43
25a
102b
102a
22b
14
MA
108
22a
154

FIG. 3A

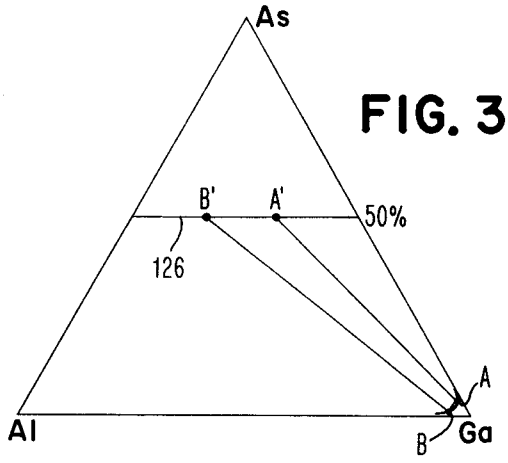


FIG. 3B

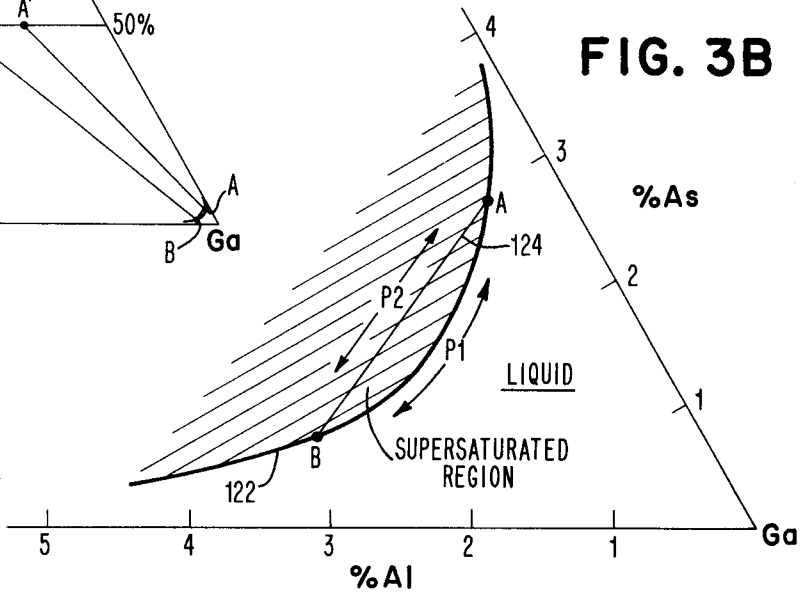


FIG. 2A

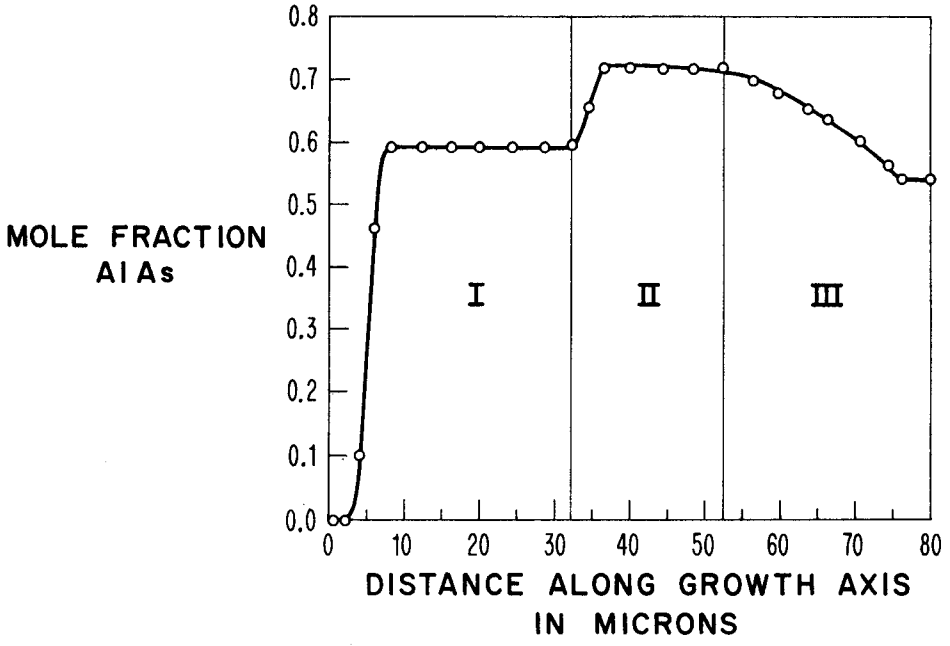


FIG. 2B

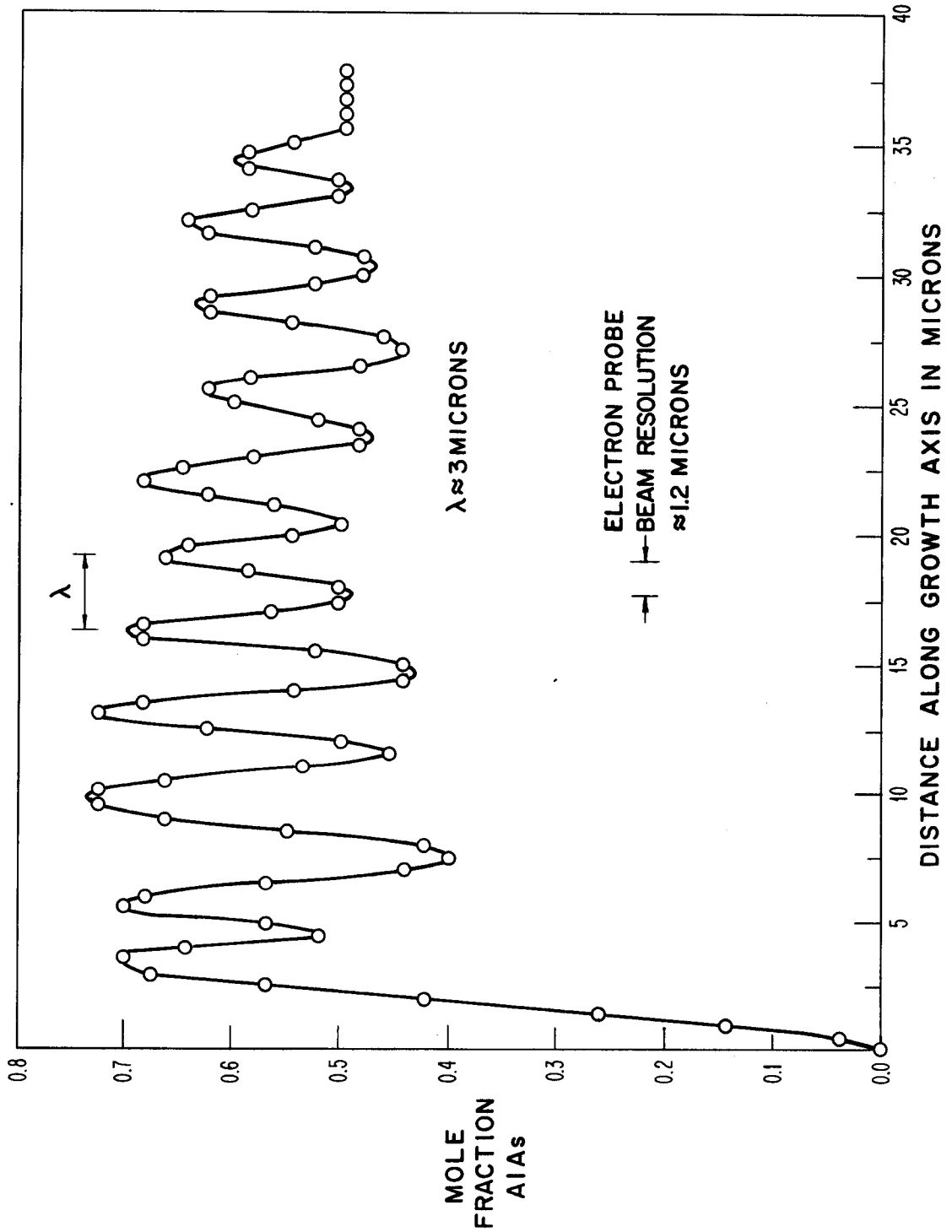

MOLE FRACTION AlAs
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
λ
λ≈3MICRONS
ELECTRON PROBE
BEAM RESOLUTION
≈1.2 MICRONS
5
10
15
20
25
30
35
40
DISTANCE ALONG GROWTH AXIS IN MICRONS

FIG. 4A

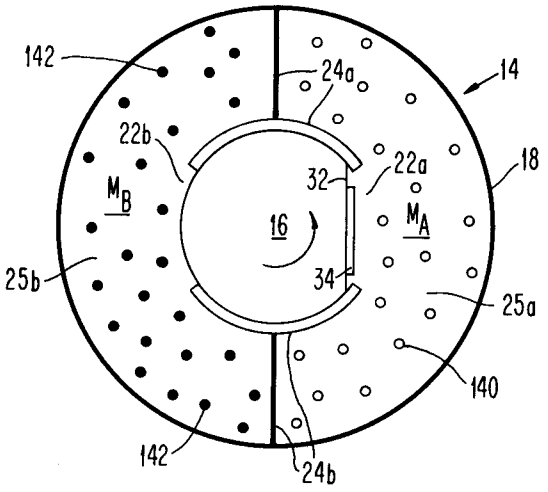


FIG. 4B

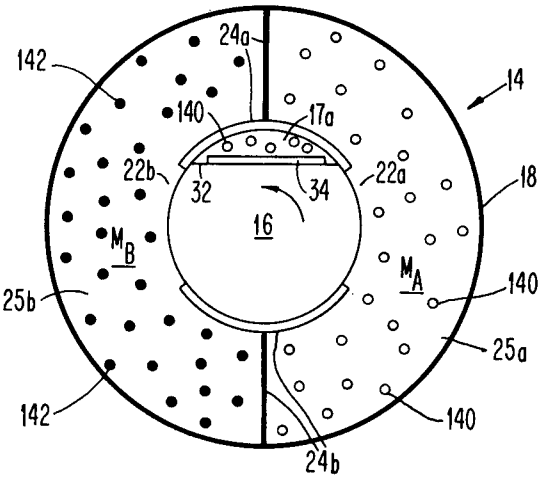


FIG. 4C

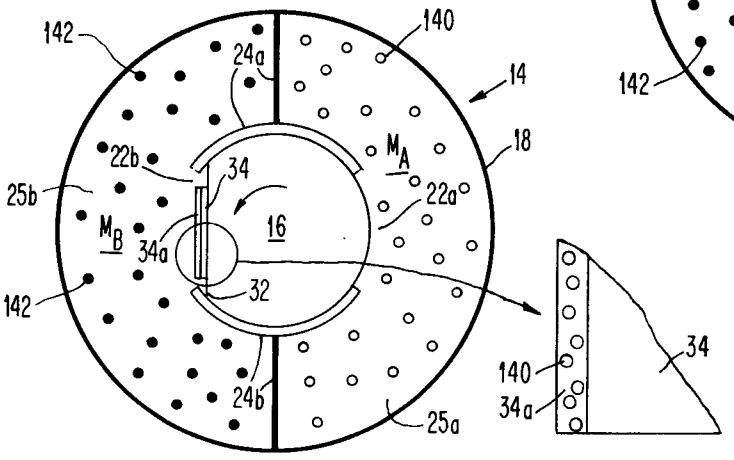


FIG. 4D

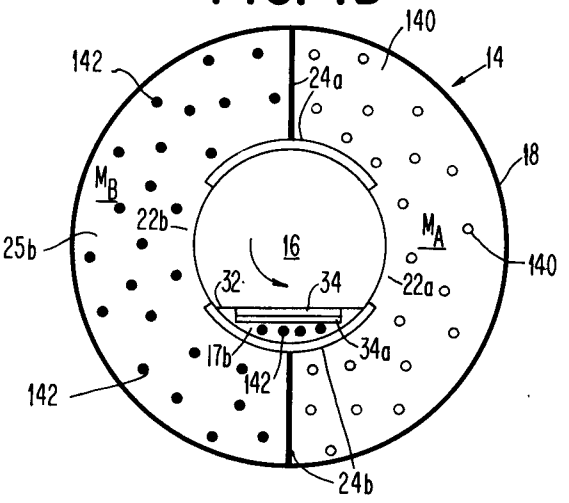


FIG. 4E

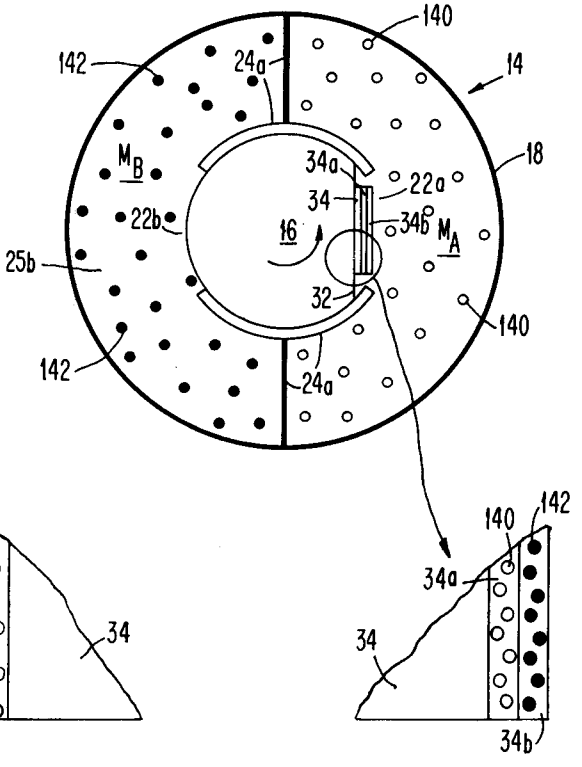
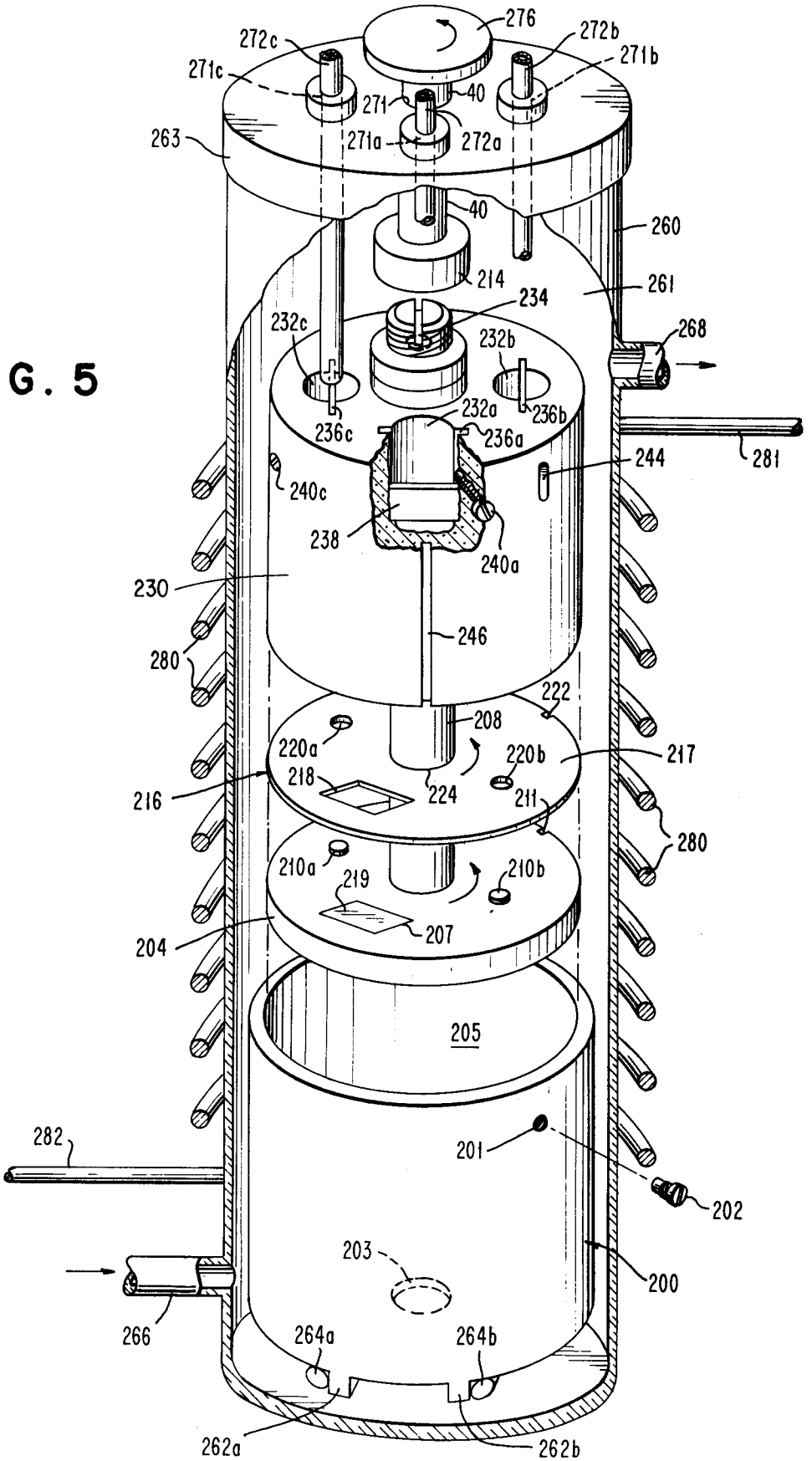


FIG. 5


276
272c
272b
271c
271b
271
40
271a
272a
263
40
260
214
261
234
232c
232b
268
232a
236c
236b
236a
281
244
240c
238
240a
230
246
280
222
208
220a
220b
217
218
224
211
216
280
210a
219
210b
204
207
205
282
201
202
203
200
266
264a
264b
262a
262b

ISOTHERMAL SOLUTION MIXING GROWTH OF SOLIDS

This is a continuation-in-part of copending application Ser. No. 84,523, filed Aug. 17, 1971, now abandoned.

BACKGROUND OF THE INVENTION

The liquid phase epitaxial method of growth has heretofore been shown to produce some superior device properties over vapor growth methods for III-V compound materials. Illustratively, GaP light emitting diodes, GaAs lasers and Si doped GaAs light emitting diodes have superior properties when formed by liquid phase epitaxy method. Recently, $Ga_{1-x}Al_xAs$ has been shown to have more desirable properties when made by the liquid phase epitaxy method.

The liquid phase epitaxial growth of $Ga_{1-x}Al_xAs$ layers has been used to realize desirable threshold current densities for injection lasers. Generally, this has been due to the use of GaAs and $Ga_{1-x}Al_xAs$ heterojunction structures. The prior art has provided a 1 μ (1 micron = 10^4 Angstrom units) thick Si doped p-type GaAs layer sandwiched between an n-type and a p-type $Ga_{1-x}Al_xAs$ layer with $0.2 \leq x \leq 0.5$. Improved performance of such devices is expected if the thickness of the p-type GaAs layer were reduced even more. Heretofore, layers 1 μ thick were grown using an apparatus in which melts of different composition were brought into contact with the surface of a substrate layer which was mechanically wiped clean of the previous melt.

The following are exemplary references which provide background material of interest for the practice of this invention:

1. Appl. Phys. Letters 11, 81 (1967), H. Rupprecht et al.
2. IEEE J. Quantum Electron. QE-4, 35 (1968), H. Rupprecht, et al.
3. IEEE J. Quantum Electron. QE-5, 211 (1969), I. Hayashi et al.
4. IEEE J. Quantum Electron. QE-5, 210 (1969), M. B. Panish et al.
5. RCA Review 30, 106 (1969), H. Kressel et al.
6. Appl. Phys. Letters 16, 326 (1970), M. B. Panish et al.
7. J. Phys. Chem. Solids, 30, 129 (1969), M. H. Panish et al.
8. 1968 Symposium on GaAS, Dallas, Texas, M. Illegems et al.
9. J. Electrochem. Soc. 116, 899 (1969), J. M. Woodall.

The background of this invention will now be discussed in greater detail. This invention relates generally to crystal growth, and it relates more particularly to crystallization of solids from liquid solutions. Precipitation from liquid solutions can occur in various ways. Common to the various ways of precipitation is supersaturation in which the liquid solution becomes supersaturated with respect to the precipitating solid. Supersaturation can occur by cooling a melt; by evaporation of a solvent; by a combination of cooling and solvent evaporation or by the change of concentration of species in a solution at a constant temperature.

Examples of crystal growth from solution by cooling alone are the liquid phase epitaxy method and the flux solution growth technique. An example of solvent evaporation is the growth of alum crystals from water solution. Illustratively, the combination of cooling and

concentration change in a melt has been used in germanium transistor technology wherein an indium dot is heated on a germanium wafer surface for causing the germanium to go into solution. When the germanium is slowly cooled, it precipitates out of solution doped with indium. As the melt cools, it slowly changes in concentration as the germanium precipitates on the germanium wafer surface. This form of alloying has been highly developed to provide growth over very large areas and is generally termed liquid phase epitaxy. An exemplary prior art application of liquid phase epitaxy has been growth of gallium arsenide crystal on gallium arsenide substrate. In this technique a gallium melt is saturated with gallium arsenide source at a given temperature and the melt is then cooled on a gallium arsenide substrate causing the precipitation of a gallium arsenide layer. An illustrative background article which describes the growth of a germanium layer on a germanium wafer by liquid phase epitaxy is RCA Review, page 603, December 1963, H. Nelson.

In the liquid phase epitaxy technique of the prior art, cooling of a melt system has been a critical requirement. Also involved in the prior art practice has been the combination of both cooling and concentration changes in the melt which naturally occur during cooling. For the liquid phase epitaxial growth of gallium arsenide on gallium arsenide substrate, the concentrations of gallium and arsenic in the liquid are constrained to change naturally as gallium arsenide is lost to the solid phase as the melt is cooled. Similarly, in solvent evaporation crystal growth, there are thermodynamic constraints on the liquid solution composition which is allowed for a given temperature as the solid crystallizes from solution.

For crystal growth of ternary compound semiconductors e.g., gallium aluminum arsenide, $Ga_{1-x}Al_xAs$, another degree of freedom for controlling solid composition was utilized. Liquid phase epitaxial growth of ternary compounds with a continuous range of compositions, e.g., $Ga_{1-x}Al_xAs$, is disclosed in co-pending application Ser. No. 646,315, filed June 15, 1967, by H. Rupprecht et al and commonly assigned, now U.S. Pat. No. 3,773,571 issued Nov. 20, 1973, and is also described in the noted article by Rupprecht et al, Appl. Phys. Letters 11 81 (1967) which relates to the contribution of the noted patent application Ser. No. 646,315 now U.S. Pat. No. 3,773,571. These references describe use of melts of predetermined composition which have been saturated and then cooled at some cooling rate to cause precipitation of some solid, e.g., gallium aluminum arsenide. Essentially, the composition of the solid has been determined or fixed by the cooling rate selected and the initial composition of the melt.

In copending application Ser. No. 860,316 filed Sept. 23, 1969, by S. E. Blum et al and commonly assigned, now U.S. Pat. No. 3,628,998 issued Dec. 21, 1971, a liquid is sandwiched between two solids which have the same composition. When the temperature of one solid is raised above that of the other solid, the solid at the higher temperature interface goes into solution and diffuses across the liquid phase and precipitates out at the other interface.

In another type of crystal growth procedure, material is introduced into a melt in such a manner as to change the composition of the melt. The introduction of a solid phase from external to a melt system to change melt

compositions is described in co-pending application Ser. No. 860,355, filed Sept. 23, 1969, by M. Lorenz and commonly assigned, now U.S. Pat. No. 3,677,836 issued July 18, 1972.

SUMMARY OF THE INVENTION

It has been discovered for the practice of this invention that when two melts at the same temperature which were separately and simultaneously saturated are mixed, the combined melt is supersaturated and crystal growth occurs isothermally. Mixing of different melts is caused to occur so as to control both composition and amount of growth of the resultant solid substance. A further technique for heterojunction growth has been discovered for the practice of this invention. The method of this invention has the capability for growing multi-layered structures with layer thicknesses substantially less than one micron.

An exemplary apparatus for the practice of this invention has a partitioned crucible which can contain two melts M_A and M_B, respectively, and a cylindrical substrate holder made of high purity and high density pyrolytic graphite. Each substrate can be brought into contact with either melt M_A or M_B by a rotation of the holder such that the substrate is aligned with one of the windows on the inner wall of the crucible. This apparatus can be used in either the normal liquid phase epitaxial growth mode or the isothermal solution mixing growth mode or both. For the isothermal mode of growth, a predetermined amount of one melt is trapped in the holder as it is rotated into the other melt. This trapped melt becomes supersaturated as it mixes with the other melt causing crystal growth.

Illustratively, A Ga-Al melt is saturated with As using a rectangular bar of undoped GaAs with a mass in excess of that required for saturation. Sufficient time should be preferably allowed for complete saturation to occur before rotating the substrate into the melt which is illustratively approximately 1 hour and 15 minutes at 830°C. If the substrate is brought into contact with the melt before this time, complete dissolution of the substrate can result.

Exemplary advantages of the invention are: the substrate wafer can be stored in the out of a window position with a small amount of melt to protect it from pitting during heat up; the growth can be interrupted by rotating the wafer to a new melt for the formation of a p-n junction, a heterojunction, or a graded band gap structure without a loss of the solid-liquid interface, a feature particularly important for the growth of $Ga_{1-x}Al_xAs$ structures; and a periodic variation in properties can be achieved for a superlattice structure, as described by L. Esaki et al in *IBM Journal of Research and Development*, 14, 61 (1970); and presented in co-pending applications Ser. No. 811,870 and Ser. No. 811,871, filed Apr. 1, 1969, and commonly assigned, now U.S. Pat. Nos. 3,626,328 and 3,626,257, respectively, issued Dec. 7, 1971.

It is an object of this invention to provide apparatus and method for growing a crystalline layer by solution growth procedure.

It is another object of this invention to provide apparatus and method for growing a crystalline layer of a semiconductor compound by liquid phase epitaxy.

It is another object of this invention to provide apparatus and method for growing a crystalline layer of a multicomponent semiconductor compound having more than two components with a continuous range of compositions by liquid phase epitaxy.

It is another object of this invention to provide apparatus and method for growing a crystalline layer of a multicomponent semiconductor compound through non-equilibrium growth by mixing of two melt systems at equilibrium at common temperatures.

It is another object of this invention to provide method and apparatus for obtaining a solid substance by non-isothermal mixing of at least two melt systems.

It is another object of this invention to provide apparatus and method for the isothermal mixing of two saturated melts to cause precipitation of a solid substance.

It is another object of this invention to provide apparatus and method for the isothermal mixing of at least two melt systems for obtaining a solid substance wherein the solid substance may be polycrystalline, amorphous or single crystal where these can be either alternating layers homogeneous in doping or alternating layers homogeneous in composition; wherein the solid substance may be semiconductor material where the semiconductor material may be elemental, two component or more than two component, where the two component system may be a compound or an alloy; wherein the two component system may be a compound or a mixed crystal system of the type III–V or II–VI or a non-compound type alloy.

It is another object of this invention to provide apparatus and method for growing a layered structure including a plurality of continuous and sequential layers of a multicomponent compound having a continuous range of compositions. This is accomplished by establishing a given multicomponent compound having a particular composition in a melt system and establishing another multicomponent compound having another particular composition in another melt system and thereafter sequentially and alternately causing a solid substrate to be transferred between said mixed melt systems to cause deposition from each said mixed melt system respectively of a solid phase consisting of the non-equilibrium combination of quantities of melts from each said system.

It is another object of this invention to provide apparatus and method for controlling the composition and structure of a solid layer.

The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of preferred embodiments of the invention, as illustrated in the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1A, 1B and 1C illustrate apparatus of a preferred embodiment of this invention for growing a multi-layered structure by isothermal solution mixing wherein two isolated melt systems are capable of being intermixed by transfer of a small incremental volume from each to the other; wherein FIGS. 1A and 1B show the apparatus in vertical section and in horizontal section, respectively; and wherein FIG. 1C shows a partially sectioned perspective view of an entire device during assembly.

FIGS. 2A and 2B present data graphs illustrating the growth of a multi-layered structure in accordance with the principles of this invention, indicating the mole fraction composition versus distance along the growth

axis for two different modes of operation of the invention.

FIGS. 3A and 3B present an idealized thermal phase diagram for the mixed crystal system $Ga_{1-x}Al_xAs$ wherein FIG. 3A shows a liquidus line for a given temperature and FIG. 3B shows a portion of 3A enlarged.

FIGS. 4A, 4B, 4C, 4D and 4E show an illustrative rendition of FIG. 1B for showing how a multilayered structure is provided by the isothermal solution mixing wherein sequential positions of the substrate holder are indicated respectively.

FIG. 5 is an exploded assembly drawing of apparatus for practice of another embodiment of this invention.

PREFERRED EMBODIMENT OF THE INVENTION

The preferred embodiment of this invention will be described with reference to FIGS. 1A, 1B and 1C. Through the description of the nature of these figures, the method and apparatus in accordance with the principles of this invention will be made clear. The apparatus of the preferred embodiment is presented somewhat schematically in vertical section in FIG. 1A and in horizontal section in FIG. 1B; and is presented in a detailed assembly in FIG. 1C shown during an initial phase of the procedure. With reference to FIGS. 1A and 1B, there is a crucible **14** and a substrate holder **16** rotatably mounted therein. The crucible **14** has outer wall **18,** inner wall **20,** windows **22** and bottom **19.** Partitions **24**a and **24***b* divide the entire crucible into two separate compartments **25***a* and **25***b*. Substrate holder **16** comprises cylinder **30** and substrate holder mount area **32** which supports substrate **34.** Slot **36** in substrate holder **16** into which a pin through hole **22***a* or **22***b* holds substrate holder **16** into place but allows rotation in crucible **14.** Vertical slot **29** allows venting of area **32.** Crucible **14** and substrate holder **16** are accessed by fastening shaft **40** to outside the system by using nut **38** onto screw **39.** The crucible **14** contains melt M_A of one composition and melt M_B of another composition. For operation of the apparatus of the preferred embodiment of this invention, substrate holder **16** is inserted into the volume **43** on the inside of inner wall **20.** The substrate area mount **32** is such that with proper rotation it lines up window area **22** such that melt M_A or M_B comes in contact with substrate **34.** Substrate holder **16** can be rotated such that substrate **34** can be aligned with window **22***b* in melt M_B or with window **22**a in melt M_A.

The operation of the apparatus of the preferred embodiment will now be described for the practice of this invention. Substrate **34** is loaded into slot **32** substrate holder **16** is then inserted adjacent to wall **20** and is fastened into place by pinning through hole **42** into slot **36.** Melt M_B is loaded into chamber **25***b* and melt M_A is loaded into chamber **42***a*. Gallium arsenide sources **44***a* and **44***b* are placed into the bottoms of chambers **25***a* and **25***b* and pinned thereon, by pins not shown. Cylinder **30** is rotated such that substrate wafer **34** is not in contact or not aligned with window area **22***a* or **22***b*. The assemby illustrated in FIGS. 1A and 1B is established in a vacuum chamber not shown in these figures but shown in detail in FIG. 1C.

With reference to FIG. 1C, the chamber **150** contains crucible apparatus **10,** and has inlet port **154,** outlet port **152,** doping tubes **156***a* and **156***b*, shaft tube **160** and holding slots **162***a* and **162***b*. The crucible assembly is loaded into quartz tube **150,** gas inlet supplies are attached to inlet port **154** and a vacuum system is attached to outlet port **152.** The gas inlets provide high purity hydrogen gas to the system and the vacuum system provides a vacuum of approximately 1 micron of mercury or less. The apparatus is assembled so that there are doping tubes **156***a* and **156***b* which have vacuum seals at openings **167***a* and **167***b*. The shaft **40** is connected to the outside of the chamber **150** through shaft tube **160** through a vacuum seal at shaft tube **160.** The entire system is then either flushed with hydrogen or vacuum baked at some temperature below growth temperature and subsequently flushed with hydrogen.

The nature of operation of the apparatus of the preferred embodiment for the growth of multi-layered structures in accordance with the principles of this invention will now be described in greater detail with reference to FIG. 1C which shows an assembly drawing of the apparatus as it is being assembled for operation.

The crucible consists of two pieces: a cylindrical piece **14** has three chambers in it, **25***a*, **25***b* and **43**; a barrel shaped piece **16** fits into the center of the chamber **43.** The cylinder **14** has two separate melt chambers **25***a* and **25***b*. The melt chambers **25***a* and **25***b* are connected to the center chamber **43** by windows **22***a* and **22***b*. Two key ways **162***a* and **162***b* on the outside of the holder **14** hold it with respect to the quartz tube **150.** Two threaded holes **19***a* and **19***b* and two pin screws **22***a* not shown are used to hold source materials not shown in place in the respective chamber **25***a* and **25***b*. The cylindrical barrel section **16** fits into the center chamber **43** and has an area **32** thereon to hold the substrate wafer **34** in place. A slot **36** on substrate holder **16** allows rotation but restricts vertical movement by an insert pin, not shown. There is a threaded portion attaching shaft **40** via nut **38** to the substrate holder **16.** A vent slot **31** allows venting of the wafer chamber. The prepared substrate wafer **34** is inserted into the area **32.** The substrate wafer **34** is positioned so that it faces the partition area. The source material is appropriately cleaned and positioned so that the pin screws can hold the source material bars in place during the run.

Appropriate materials are placed into the chambers **25***a* and **25***b*. Doping may be added at this time or dropped in later via tubes **156***a* and **156***b*. With the pin screws in place, the substrate holder **16** is free to rotate but is not free to move vertically with respect to the crucible **14.** The shaft **40** is then connected by nut **38** to the assembled crucible and the entire assembly lowered into the chamber **151** so that the key ways **102***a* and **102***b* on the quartz tube **150** are engaged in key way slots **162***a* and **162***b* on the crucible. This allows rotation of the center barrel **16** and prevents rotation of the outer crucible **14.** With the substrate wafer **34** in the neutral position, i.e., it is interfacing section **24,** the system is evacuated, baked at a low temperature, and then back filled with hydrogen. The hydrogen flush is continued throughout the entire growth schedule in accordance with the principles of this invention. The system is then heated to appropriate temperature between 750°C and 950°C and an appropriate soak time is allowed to let the solutions M_A and M_B equilibriate. The substrate holder **16** is rotated 90° into one of the windows **22***a* or **22***b*. Melt from the particular crucible chamber **25***a* or **25***b* flows into the substrate chamber and growth is initiated by cooling the furnace at an appropriate rate, e.g., between 0.03°C/min. and

30°C/min. When a desired first growth has been accomplished, cooling may be continued after rotating the crucible holder into the other window or cooling may be ceased and isothermal growth may be continued by sequential rotations from window **22***a* to window **22***b*. After desired growth is accomplished, the substrate holder **16** is rotated to a neutral position, i.e., it faces the area **24** of the crucible, and the power is turned off to the furnace winding **104** via terminals **106** and **108.** The crucible assembly **10** is normally left in this condition until it has cooled to room temperature.

FIG. **2A** shows the composition profile of mole fraction of AlAs vs distance in microns as measured along the growth axis of an exemplary layer grown by liquid phase epitaxy in accordance with the principles of this invention in which there was only one rotation between melt M_A and melt M_B. The zero position of this plot at zero microns corresponds to the interface between the gallium arsenide substrate and the GaAlAs epitaxial layer. The layer profile is broken up into three regions designated I, II and III. Region I was grown out of a relatively low aluminum composition melt, region II was grown out of a relatively high composition aluminum, and region III which results from cooling the region II at a higher than equilibrium cooling rate. It should be noted that region I is homogeneous in composition and region II is relatively homogeneous in composition, whereas region III has a large variation in composition. In accordance with the principles enunciated in copending application Ser. No. 646,315 filed June 15, 1967 and commonly assigned, now U.S. Pat. No. 3,773,571 issued Nov. 20, 1973, when the furnace is shut off, the cooling rate starts out slowly and goes through some maximum value as the furnace cools faster and faster. Therefore, the aluminum concentration drops off strongly with increasing cooling rates as shown in region III.

Region I is accomplished by normal cooling, region II is accomplished by normal cooling after rotation from melt M_A and melt M_B, and region III is the result of extremely fast cooling to room temperature after rotation from melt M_B to storage position. The 80 micron position is the surface edge of the final growth layer. The data was obtained by using a conventional electron beam probe analyzer which X-ray fluoresces a sample with an electron beam with a dimension of approximately 1½ to 2 microns resolution. The X-ray fluorescent data is recorded on a counter which is then converted through calibration factors into mole fraction AlAs.

FIG. **2B** presents data representation of mole fraction AlAs plotted vs. distance in microns in the growth direction for a layered structure grown by the isothermal melt mixing procedure of this invention in which there are peaks which correspond to the compositions which occur as a result of rotation from M_B into M_A and valleys which correspond to the composition of the layer which is formed by a rotation of M_A into M_B. Ideally, the interface of the sequential layers begins at the average composition between the peaks and the valleys so that all of the area under the average value represents a layer of M_A and everything above the average value represents a layer of M_B. This demonstrates that the growth occurs as a result of the mixing of two melts since the temperature was held constant for approximately 20 revolutions. FIG. **2B** is not an idealized square wave profile because of the resolution of the electron beam probe. Both the amplitude and the peak and valley compositions approach each other as the result of dilution of the melts M_A by melt M_B and of melt M_B by melt M_A upon rotation of the substrate holder **16** which causes the melt mixing.

PRACTICE OF THE INVENTION

The composition profiles along the growth axis for two types of growth procedure according to the principles of this invention are shown in FIGS. **2A** and **2B**. FIG. **2A** shows the profile of a layer which was grown from two different melts at a growth rate of 0.1°C/min. with the apparatus shown in FIGS. **1A**, **1B** and **1C**. The layer was grown on the (**100**) face of an undoped GaAs substrate **34.** The first part of the layer was grown from an As saturated melt M_A containing 30 gms Ga with an Al/Ga weight ratio of 3×10^{-3}, and cooled from 862°C to 852°C. The substrate was then rotated into a melt M_B containing 30 gms Ga with an Al/Ga weight ratio of 5×10^{-3}, and cooled between 852°C and 842°C. The composition profile is very flat for the part of the growth which occurs in each melt. The decrease in Al concentration which occurs near the end of the profile is due to fast freezing of the melt which is trapped in the substrate holder when the furnace is turned off.

FIG. **2B** shows the composition profile of a multilayer structure grown in the isothermal solution mixing mode of this invention by several rotations between two melts, M_A and M_B. The layers have a periodic variation in Al concentration along the growth axis with an overall decrease in amplitude along the growth axis. The peak-to-peak spacing is about 3 microns and each sub-layer is about 1.5 microns thick. One melt M_A had an Al/Ga ratio of 10^{-3} and the other melt M_B had a ratio of 5×10^{-3}. Rotation was accomplished by rotating the substrate holder **16** in less than 1 sec. time period from one melt to the other melt and holding thereat for approximately 3 minutes. In other experiments it was found that the thickness and spacing of the sub-layer structure was independent of cooling rate in the range between zero and 0.1°C/min. and of rotation cycle time between melts M_A and M_B in the range between 3 min./melt and 30 sec./melt. This is evidence that the growth of the substrate is due to the supersaturation which occurs during the mixing of the trapped melt which is brought over by the substrate holder in contact with the other melt.

The volume ratio of the melt in compartment **25**a or **25**b to the melt trapped in the holder and transferred from one melt compartment to the other is **25.** By the proper selection of this volume ratio, the growth temperature and the melt volume, it is possible to grow any desired thickness of a sublayered structure. Illustratively, the apparatus and method of this invention have been utilized to grow a heterojunction layered structure in which the $Ga_{1-x}Al_xAs$ layers are 1 micron thick and the GaAs p-type layer is 1 micron. This structure has produced lasing thresholds of 3,600 A/cm² at room temperature at a 10^{-4} duty cycle and 6,000 A/cm² at a 10^{-2} duty cycle.

EXPLANATION OF THE INVENTION

A theoretical explanation of the isothermal solution mixing epitaxial growth according to the principles of this invention follows from recognition of certain isothermal phase boundary-composition relations in the $Ga_{1-x}Al_xAs$ system. The phase diagram for the Ga_{1-x}-

Al_xAs ternary mixed crystal system has been discussed in the literature of which the following are exemplary articles:

a. J. Phys. Chem. Solids, 30, 129 (1969), M. H. Panish, et al.

b. 1968 Symposium on GaAs, Dallas, Texas, M. Illegems et al.

With reference to the ternary phase diagram of FIG. 3A examination of the Ga rich portion of this system shows that a solid-liquid phase boundary **122** exists over a large solid composition range **126**, and that an isothermal liquidus curve **122** is such that when two melts M_A and M_B having different composition on the liquidus line are mixed, the mixed melt will be supersaturated and hence crystallization can occur. FIG. **3B** schematically presents the Ga-Al-As liquidus line **122** at constant temperature T at the Ga rich corner of the phase diagram. The points A and B represent two melts M_A and M_B of different composition at solid-liquid equilibrium. Under equilibrium conditions, the composition of the liquid melt can change along path P_1 of liquidus line **122** between points A and B. When the melts M_A and M_B are mixed, the final composition of the mixed melt will lie at some point along path P_2 indicated as line **124** connecting points A and B, the actual point depending on the volume ratio of the two melts. However, any point along path P_1 along line **124** at temperature T except for points A and B lies in a region of supersaturation. This supersaturation is relieved by the growth of $Ga_{1-x}Al_xAs$ crystal. In FIG. **2A**, for a melt of composition A the corresponding solid is indicated as A'; and for a melt of composition B, the corresponding solid is indicated as B'.

As will be described in detail hereinafter with reference to FIGS. **4A**, **4B**, **4C**, **4D** and **4E**, the composition of the solid which grows during isothermal melt mixing at one chamber more closely corresponds to the melt transported from the other chamber than to the melt at the growth window.

The operation of this invention can be visualized by considering an idealized set of circumstances shown schematically in FIGS. **4A**, **4B**, **4C**, **4D** and **4E**. These figures show in somewhat schematic form the horizontal view of the apparatus of FIG. **1B** in five different sequential positions.

When the apparatus of FIGS. **1A**, **1B** and **1C** is used in the isothermal melt mixing mode according to the principles of this invention, the flow of the solution of melt mixing that occurs and resulting crystal growth can be visualized by considering a sequence of events illustrated in FIGS. **4A**, **4B**, **4C**, **4D** and **4E**. At the beginning, as shown in FIG. **4A**, the substrate wafer **34** is aligned in contact with melt M_A at window **22***a*. The composition of the melt M_A is homogeneous in all regions of the crucible compartment **25**a since the melts M_A and M_B have been established in equilibrium at the temperature for the isothermal melt mixing. The solid composition corresponding to melt M_A is represented by circles **140**. The solid composition corresponding to melt M_B is represented by the dots **142**. The crucible holder **16** is then rotated into the position shown in FIG. **4B** where a volume **17***a* of melt M_A is trapped between the substrate holder **16** and the wall of the compartment **24***a*. The volume **17***a* of melt M_A is then moved by substrate holder **16** to window **22***b* in contact with melt M_B in chamber **25***b*, as shown in FIG. **4C**.

At first, the melt M_B has an interface with the volume **17***a* of melt M_A which has been moved to window **22***b*. Since melt M_B has a different concentration than volume **17***a* of melt M_A, an interdiffusion mechanism occurs; i.e., melt M_A that was transported by the substrate holder **16** starts mixing with the bulk of the melt M_B in crucible chamber **25***b*. As this occurs, the melt M_A which is next to the substrate wafer **34** becomes supersaturated which is relieved by crystal growth having a composition **140** on the substrate surface. It has been determined that the composition **140** of the layer **34**a which deposits on the substrate **34** corresponds to the composition to be expected from equilibrium growth from a melt having the composition M_A. After the volume **17***a* of melt M_A has completely mixed with the melt M_B in the crucible chamber **25***b*, there is a stable system in crucible chamber **25***b* and no further crystal growth occurs. The incremental amount that melt M_B has changed in concentration depends on the volume of the melt M_A present therein and the composition of the melt M_A which was transported by crucible holder **16** from chamber **25***a*.

Ideally, only melt M_A is deposited as layer **34***a*. Actually, a certain amount of melt M_A has mixed with the melt M_B in crucible chamber **25***b*. A volume **17***b* of melt M_B is shown in FIG. **4D** partially transported toward crucible chamber **25***a*. Finally, the substrate holder **16** is shown rotated in FIG. **4E** such that another layer **34***b* with composition **142** has deposited on layer **34***a*. It has been determined that the composition **142** of layer **34***b* corresponds to the composition of the liquid trapped in volume **17***b* shown in FIG. **4D**.

The graph shown in FIG. **2B** substantiates the foregoing explanation of isothermal melt mixing of multilayered structures in accordance with the principles of this invention. The graph has the appearance of a damped sine wave. As noted hereinbefore, the concentration profile is actually more closely that of a rectangular wave pattern. The damping characteristic indicates that the sequential layers being deposited begin to have an increasing amount of content of the melt at the crucible chamber where growth is occurring as a consequence of a prior transport thereof to the other crucible chamber. The process may be repeated so long as there remains a distinct characteristic to the melts M_A and M_B. When equilibrium has occurred for both melt systems, no further crystal growth without cooling is observed.

ALTERNATIVE EMBODIMENT

The further practice of this invention will be described with reference to FIG. **5** which presents an alternative apparatus for the practice of this invention. It includes three melt chambers and a rotating substrate holder in a horizontal plane whereby the growth of the layered structure in accordance with the practice of this invention is accomplished isothermally without regard for any temperature gradients in the vertical axis of the growth chamber.

The apparatus illustrated in FIG. **5** comprises a outer crucible **200** with inner volume **205**, feet **262***a* and **262***b*, a tapped hole **201** and retaining screw **202**. The outer crucible **200** fits into the bottom of the quartz chamber **260** and does not rotate with respect thereto. It also houses the other components of the crucible. The substrate wafer holder **204** consists of a flat disk structure with a depression **207** to house the wafer, two

tapped holes with retaining screws **210***a* and **210***b*, a bottom projection not shown which rides in cylindrical depression **203** in the bottom of outer crucible **200**, a venting slot **211**, and a vertical shaft **208** ending in threaded portion **212**. The substrate wafer retainer and spacer **216** has center hole **224** which fits over shaft **208**, a through window **218** slightly smaller than the wafer, two through holes **220** which are 180° apart and are 90° from the through window, and a vent slot **222**. Barrel **230** with center hole **242** fits over shaft **208**. It has three melt chambers, **232***a*, **232***b* and **232***c* with key slots **236** which extend approximately two-thirds of the way down the barrel. Retaining screw **240** stops a source material bar **238** from rising in the melt after it has been inserted in the slto **236**. A vent slot **246** extends the length of the barrel **230** and a vent hole is positioned at one of the four 90° positions on the same radius as the melt chambers **232***a*, **232***b* and **232***c*. A stop slot **244** which receives stop screw **202** and maintains the position of the barrel so that it does not rotate with respect to part **200**. A nut **214** is fastened to the top of shaft **208** and holds the crucible turning quartz rod **40** to shaft **208**.

The growth chamber within which the growth apparatus is established will now be described. A quartz cylinder **260** with a flat bottom, has with two stop rods **264***a* and **264***b* at the bottom to hold the outer crucible with respect to itself. An inlet tube **266** and exit tube **268** are attached to the quartz cylinder. This is then fitted with a vacuum seal fitting **263**. The quartz rods **264***a* and **264***b* are parallel to the bottom of the quartz tube **260** and are spaced so projections **262***a* and **262***b* from the outer retainer crucible **200** fit between the rods and do not allow rotation of the outer crucible. The vacuum seal fitting **263** has four smaller vacuum connectors on the top thereof: one seal **271** at the center and the other three seals **271***a*, **271***b* and **271***c* are placed 90° apart from each other on the same radius as the melt chambers in barrel **230**. The vacuum seal fitting is oriented so that the dopant drop tubes **272***a*, **272***b* and **272***c* via seals **271***a*, **271***b* and **271***c* respectively are above the desired respective chambers **232***a*, **232***b* and **232***c*.

The manner in which the apparatus shown in exploded form in FIG. **5** is assembled for operation for growth of a layered structure in accordance with the principles of this invention will now be described. The prepared substrate wafer is placed in the wafer chamber **207** on the surface of wafer support **204**. The wafer retainer and spacer **216** is positioned over the shaft **208** so that the window **218** is over the wafer and retains it and forms the melt storage volume equivalent to volume **17** in FIG. **4**. The two stop screws **210** are brought flush to the surface of the wafer retainer and spacer **216**. Care must be taken that the stop screws **210** do not extend above the plane of the surface **217** of spacer **216** where they would interfere with the rotation thereof relative to the barrel **230**. The barrel **230** with its center hole **242** slides over shaft **208** and is positioned such that the vent hole **234** is above the wafer **219** and the wafer window **207**.

The source materials **238***a*, **238***b* and **238***c* are put in the appropriate slots **236***a*, **236***b* and **236***c* and are retained below the surface of the melt by retaining screw **240***a*, **240***b* and **240***c*, respectively. The subassembly parts **204**, shaft **208**, substrate support **216** and the barrel **230** are then placed in the cylindrical opening **205** of outer crucible **200** and retained there by the retaining screw **202** in the threaded hole **201** via slot **244** in barrel **230**. As assembled, the barrel **230** and the outer crucible **200** are fixed with respect to each other. The shaft **208**, wafer holder **204** and the retaining spacer **216** are immobile with respect to each other but free to turn with respect to the barrel **230** and the outer crucible **200**. When the vent hole **234** is aligned with the wafer window **218** and wafer **219**, there is then an entire vent slot consisting of partial vent slots **246**, **222** and **211**. The entire vent slot formed by partial vent slots **246**, **222** and **211** allows the bottom cylindrical opening **203** under substrate support **204** to be vented. The wafer-holding support **204**, shaft **208**, spacer retainer **216** and barrel assembly **231** are placed into the hole **205** of the outer crucible **200**. The screw **202** is then inserted into slot **244** of barrel **230** and prevents rotation of barrel **230** with respect to outer crucible **200**.

The quartz rod **40** is connected to the crucible assembly and is used to lower the assembled crucible into the chamber **261** of quartz container **260**. The appropriate melts are placed in the respective melt chambers **232***a*, **232***b* and **232***c* and the crucible assembly is ready to be inserted into the quartz container **260**. When the crucible assembly is in the bottom of the chamber **261**, two quartz rods **264***a* and **264***b* position it and keep it from turning with respect to the quartz ware. The fitting and seal **263** for the top of the quartz container **260** is then placed in position, with the drop tubes **272***a*, **272***b* and **272***c* being loaded with the appropriate dopants over the respective melt chamber **232***a*, **232***b* and **232***c*. The system inlet and outlet ports **265** and **267** are then fastened to the hydrogen input and the vacuum line, not shown. After the appropriate flush time has elapsed, the hydrogen line is turned off and the vacuum line opened so that the entire system including the hydrogen line is evacuated. During this period, the vent hole **234** is positioned over the wafer **219** and venting of the chamber **203** volume is accomplished. The slots **246**, 222 and **211** were previously aligned so that the venting of the entire crucible assembly is now possible. When the vacuum pressure reaches approximately one of micron Hg, the entire unit is heated to between 200°–250°C by furnace windings **280** which one electrically energized via input and output terminals **281** and **282** from a power source, not shown. Temperature of the apparatus is maintained for approximately 15 minutes and the vacuum line is then closed and the system is back filled with hydrogen and a hydrogen flush is maintained throughout the entire run. The furnace **280** is then brought to temperature and the crucible assembly **259** and growth materials in chambers **232***a*, **232***b* and **232***c* are soaked for an appropriate length of time, usually about an hour to an hour and one half. After this period the first rotation is accomplished. The shaft **40** via knob **276** is rotated 90° so that the wafer holder **204** and the spacer retained **216** are moved into the first melt position. If desired at this time, dopants could be added to the first melt.

The furnace is now cooled at approximately 0.1°C per minute for an appropriate period of time, depending on the thickness of the desired layer. The heating and cooling cycle program is then shut off and the rotations of shaft **40** are initiated for isothermal solution growth according to the principles of this invention. Illustratively, there is a rotation of 90° into the second

melt at chamber **232***b* where there is a hold for 30 seconds to three minutes depending on the amount of growth selected, and then a rotation back to the melt at chamber **232***a*. This mode of rotation is continued until the selected number of layers is achieved. After the final rotation back to chamber **232***a*, a cooling program is then continued for approximately 30 minutes at a rate of 0.1°C/min. After this cooling period, the wafer **219** is rotated to a neutral position, e.g. a 45° rotation, and the power turned off to terminal **281** and **282** of the furnace **280.**

For another mode of growth, the cooling program is not shut off after the initial cooling period, but continued during rotation of the substrate holder **204** into the second melt. Dopant may now be dropped in the second melt. After an appropriate cooling time in the second melt, the wafer is rotated to a neutral position. For still another mode of solid growth three melts in chambers **232***a*, **232***b* and **232***c* may be utilized after the growth is finished in the second melt. There is rotation of the substrate holder **204** into the third melt for a short period of time with finally there is rotation into a neutral position and turning off of the power to the furnace. The thir melt is used to terminate growth so that a fast growth layer does not appear on the surface of the multi-layer structure. After the termination of the run, the crucible assembly and quartz container **260** are normally left in the furnace windings **280** under hydrogen flush until both have cooled to room temperature.

EXEMPLARY DESIGN CONSIDERATIONS

As disclosed for the concept of this invention, in a ternary liquid system it is often possible to find two different compositions, both of which are on the liquidus curve at a given common temperature, such that when these two compositions are mixed the melt will become supersaturated. For the gallium aluminum arsenide system, if at the same temperature, a ternary alloy of gallium aluminum arsenide containing a greater amount of gallium arsenide is mixed with a similar alloy containing a greater amount of aluminum arsenide, growth of the alloy, gallium aluminum arsenide, will take place on a substrate provided for this growth.

Clearly to one of ordinary skill in the art of crystal growth, the principles of this invention have a wider range of application. Through knowledge of the phase diagrams of other III-III-V materials, it is recognized that the isothermal solution mixing growth of materials may be accomplished according to the principles of this invention for all these materials. For those III-III-V systems for which the phase diagrams have not actually been observed in the laboratory, calculations exist which show that they have the same type of phase diagrams. Examples of these III-III-V alloys are $Ga_{1-x}In_xAs$ and $Ga_{1-x}Al_xP$. Antimony can be substituted for phosphorous. Therefore, III-III-V materials can be grown by the process of this invention. Other semiconductor alloy materials which obey the same relationship are the II-II-VI materials. An example of such materials is $Zn_xCd_{1-x}Se$. The selenium can be substituted with either sulfur or tellurium thereby forming a class of such materials.

It is also clear to one of ordinary skill in the art of crystal growth that the principles of this invention are not limited to the growth of semiconductor materials. There are also many electrooptic materials which are ternary alloys. An example is the $KNbO_3$-$LiNbO_3$-$BaNb_2O_6$ system for which the ternary phase diagram has been published by E. A. Giess et al, Materials Research Bull. 5, 109–116 (1970), especially FIG. **1.** The liquidus curves show sufficient curvature that it is clear that a high degree of supersaturation can be obtained upon the mixing of two appropriate liquid components. Thus, crystal growth will occur by the method of this invention in this and similar materials. Similar behavior is predictable in the Na_2O-BaO-Nb_2O_5 system published by E. A. Giess et al, J. Am. Ceramic Soc. 53, 14–17 (1970), especially FIG. **1.**

Magnetic metal oxide systems have been described in the literature in considerable detail such as the Fe_2O_3-Y_2O_3-Al_2O_3 system as published by H. J. van Hook, J. Am. Ceramic Soc. 46, 121–124 (1963), especially FIG. **1.** The garnet and orthoferrite phases show substantial curvature of the liquidis curves. Hence, it is predictable according to the principles of this invention that they may be grown by the isothermal solution mixing growth process of this invention. The liquidus curves for the spinel and corundum phases show much less curvature and hence the principles of this invention would be somewhat less applicable to their growth.

Another example for the practice of this invnention is the Fe_2O_3-FeO-$YFeO_3$ system as published by H. J. van Hook, J. Am. Ceramic Soc. 45, 162–165 (1962), especially FIG. **4.** The garnet phase shows considerable curvature. The magnetite phase shows even greater curvature. The orthoferrite phase shows some curvature and the hematite phase very little, if any, curvature. Therefore, the garnet and magnetite phases can be easily grown according to the principles of this invention. The orthoferrite phase can be grown with some difficulty, but the hematite phase cannot be grown. However, these statements apply only within the range of temperatures measured, i.e., less than 1,600°C.

It is recognized from the foregoing recitation of exemplary design considerations that the practice of this invention has several aspects.

In the practice of one aspec of this invention, there is the method for growing a solid structure comprising the steps of: established respective regions of two liquid substances each at thermal equilibrium at a respective temperature, said liquid substances being different members of a multicomponent compound system with more than two components and with a continuous range of compositions, and when mixed providing a supersaturated solution; establishing a substrate adjacent one said liquid substance at a solid-liquid interface: transferring an incremental volume of said one liquid substance adjacent to said substrate at said solid-liquid interface together with said solid thereat to a liquid-liquid interface with said region of said other liquid substance; and depositing said solid structure on said solid-liquid interface by isothermal solution mixing of said incremental volume of said one liquid substance with said region of said other liquid substance. In greater detail, the respective regions of said two liquid substances are each at thermal equilibrium with respect to a respective solid phase with a related composition at a given temperature. Further, the multicomponent compound system can be the III-III-V ternary semiconductor compound system. In particular, the multicomponent compound system is $Ga_{1-x}Al_xAs$ where $0 < X < 1$.

In the practice of another aspect of this invention, there is the method for growing a solid structure comprising the steps of: establishing respective regions of two liquid substances each at thermal equilibrium with respect to a respective solid phase with a related composition at a respective temperature, said liquid substances being different members of a multicomponent compound system with more than two components and with a continuous range of compositions, and when mixed providing a supersaturated solution; establishing a substrate adjacent one said liquid substance at a solid-liquid interface; transferring an incremental volume of said one liquid substance adjacent to said substrate at said solid-liquid interface together with said solid thereat to a liquid-liquid interface with said region of said other liquid substance; and depositing said solid structure with substantially said solid phase composition related to said one liquid substance on said solid-liquid interface by solution mixing of said incremental volume of said one liquid substance with said region of said other liquid substance which provides a supersaturated solution from which said solid structure is deposited.

We claim:

1. Method for growing a solid structure comprising the steps of:

establishing respective regions of two liquid substances each at thermal equilibrium with respect to a respective solid phase with a related composition at a respective temperature, said liquid substances being different members of a multicomponent compound system with more than two components and with a continuous range of compositions, and when mixed providing a supersaturated solution;

establishing a substrate adjacent one said liquid substance at a solid-liquid interface;

transferring an incremental volume of said one liquid substance adjacent to said substrate at said solid-liquid interface together with said solid thereat to a liquid-liquid interface with said region of said other liquid substance; and

depositing said solid structure with substantially said solid phase composition related to said one liquid substance on said solid-liquid interface by isothermal solution mixing of said incremental volume of said one liquid substance with said region of said other liquid substance which provides a supersaturated solution from which said solid structure is deposited.

2. Method for growing a solid structure comprising the steps of:

establishing respective regions of two liquid substances each at thermal equilibrium at a respective temperature, said liquid substances being different members of a multi-component compound system with more than two components and with a continuous range of compositions, and when mixed providing a supersaturated solution;

establishing a substrate adjacent one said liquid substance at a solid-liquid interface;

transferring an incremental volume of said one liquid substance adjacent to said substrate at said solid-liquid interface together with said solid thereat to a liquid-liquid interface with said region of said other liquid substance; and

depositing said solid structure on said solid-liquid interface by isothermal solution mixing of said incremental volume of said one liquid substance with said region of said other liquid substance.

3. Method as set forth in claim **2** wherein said liquid substances are dilute solutions.

4. Method as set forth in claim **2** wherein said respective regions of said two liquid substances are each at thermal equilibrium with respect to a respective solid phase with a related composition at a given temperature.

5. Method as set forth in claim **2** wherein said substrate is crystalline and said deposited solid structure is crystalline.

6. Method as set forth in claim **5** wherein said substrate has a compatible lattice constant with said multicomponent compound system.

7. Method as set forth in claim **4** wherein said multicomponent compound system is a ternary semiconductor compound.

8. Method as set forth in claim **7** wherein said ternary compound is a III-III-V compound.

9. Method as set forth in claim **8** wherein said III-III-V compound is $Ga_{1-x}Al_xAs$ where $0 < X < 1$.

10. Method as set forth in claim **9** wherein said substrate is GaAs.

11. Method as set forth in claim **9** wherein said X of one said compound is approximately 0.7 and X of said other compound is approximately 0.5.

12. Method as set forth in claim **5** including the additional steps of:

transferring a second incremental volume of said other liquid region adjacent to said deposited crystalline solid structure together with said crystalline solid to said one liquid region at a liquid-liquid interface therewith; and

depositing another crystalline solid structure on said second solid-liquid interface by isothermal solution mixing, whereby there is grown a layered crystalline structure.

13. Method as set forth in claim **12** wherein said layered crystalline structure comprises a heterojunction formed by said one solid structure and said another solid structure.

14. Method as set forth in claim **13** wherein said heterojunction is a p-n junction.

15. Method for growing a solid structure comprising the steps of:

establishing respective regions of two liquid substances each at thermal equilibrium with respect to a respective solid phase with a related composition at a respective temperature, said liquid substances being different members of a multicomponent compound system with more than two components and with a continuous range of compositions, and when mixed providing a supersaturated solution;

establishing a substrate adjacent one said liquid substance at a solid-liquid interface;

transferring an incremental volume of said one liquid substance adjacent to said substrate at said solid-liquid interface together with said solid thereat to a liquid-liquid interface with said region of said other liquid substance; and

depositing said solid structure with substantially said solid phase composition related to said one liquid substance on said solid-liquid interface by solution mixing of said incremental volume of said one liquid substance with said region of said other liquid

substances which provides a supersaturated solution from which said solid structure is deposited.

16. Method as set forth in claim **15** wherein said substrate is crystalline and said deposited solid structure is crystalline.

17. Method as set forth in claim **16** wherein said substrate has a compatible lattice constant with said multicomponent compound system.

18. Method as set forth in claim **16** wherein said multicomponent compound system is a ternary semiconductor compound.

19. Method as set forth in claim **17** wherein said multicomponent compound is a III-III-V semiconductor compound.

20. Method as set forth in claim **19** wherein said III-III-V compound is $Ga_{1-x}Al_xAs$ where $0 < X < 1$.

21. Method as set forth in claim **17** wherein said substrate in GaAs and said multicomponent compound system is $Ga_{1-x}Al_xAs$ where $0 < X < 1$.

22. Method as set forth in claim **15** including the additional steps of:

transferring a second incremental volume of said other liquid substance adjacent to said deposited solid structure at said solid-liquid interface together with said solid structure thereat to a liquid-liquid interface with said region of said one liquid substance; and

depositing another solid structure with substantially said solid phase composition related to said other liquid substance on said solid-liquid interface by solution mixing of said incremental volume of said other liquid substance with said region of said one liquid substance which provides a supersaturated solution from which said another solid structure is deposited, whereby there is grown a layered crystalline structure.

23. Method as set forth in claim **22** wherein said layered crystalline structure comprises a heterojunction formed by said one solid structure and said another solid structure.

24. Method as set forth in claim **23** wherein said heterojunction is a p-n junction.

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