United States Patent

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[54] **METHOD FOR GROWTH OF A MIXED CRYSTAL WITH CONTROLLED COMPOSITION**
17 Claims, 7 Drawing Figs.

[52] **U.S. Cl.** **117/201,** 23/295, 23/300, 23/301, 148/1.6, 148/15, 148/171, 148/176

[51] **Int. Cl.** **B01j 7/08,** B01j 7/16

[50] **Field of Search** ..... 117/201; 23/301 SP, 295, 300; 148/1.6, 176, 15, 171

[56] **References Cited**

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ABSTRACT: A mixed crystal e.g., $Ga_xIn_{1-x}P$, of controlled composition in the growth direction, either of substantially homogeneous composition or of variable composition, is prepared from the melt or liquid solution by the method of this disclosure. Illustratively, the starting materials are two different pure III–V compounds with different melting points, e.g., GaP and InP, which are to be the components from which the mixed crystal is to be grown. A three-layered composite or charge is fabricated consisting of a layer of the lower melting compound flanked on both top and bottom by layers of the higher melting compound. The composite is established in a crucible which is sealed in a quartz ampul in vacuum to form an assembly. When an overpressure of either an inert or a reactive gas is required, the quartz ampul is sealed inside a stronger container, e.g., of graphite. The assembly is allowed to equilibrate isothermally in a furnace of a given temperature to yield a liquid solution from which the desired solid solution of mixed crystal can crystallize. For crystal growth with homogeneous composition the assembly is lowered slowly into a slightly cooler temperature zone of the furnace and crystallization of the mixed crystal occurs at the lower one of the two liquid-solid interfaces. A single crystal is obtained by epitaxial growth when the substrate is a single-crystal seed. As the liquid becomes depleted in the higher melting component at the growth interface, the dissolution of the higher melting component at the upper liquid-solid interface replenishes the composition of the liquid. This physical process is incrementally small, i.e., it occurs slowly, and results in the composition of the liquid remaining essentially in a steady state of constant composition. Illustratively, $Ga_xIn_{1-x}P$ cylindrical ingots of approximately 1 cm. length × 1.5 cm. diameter are readily produced from the components of GaP and InP by the practice of this disclosure.

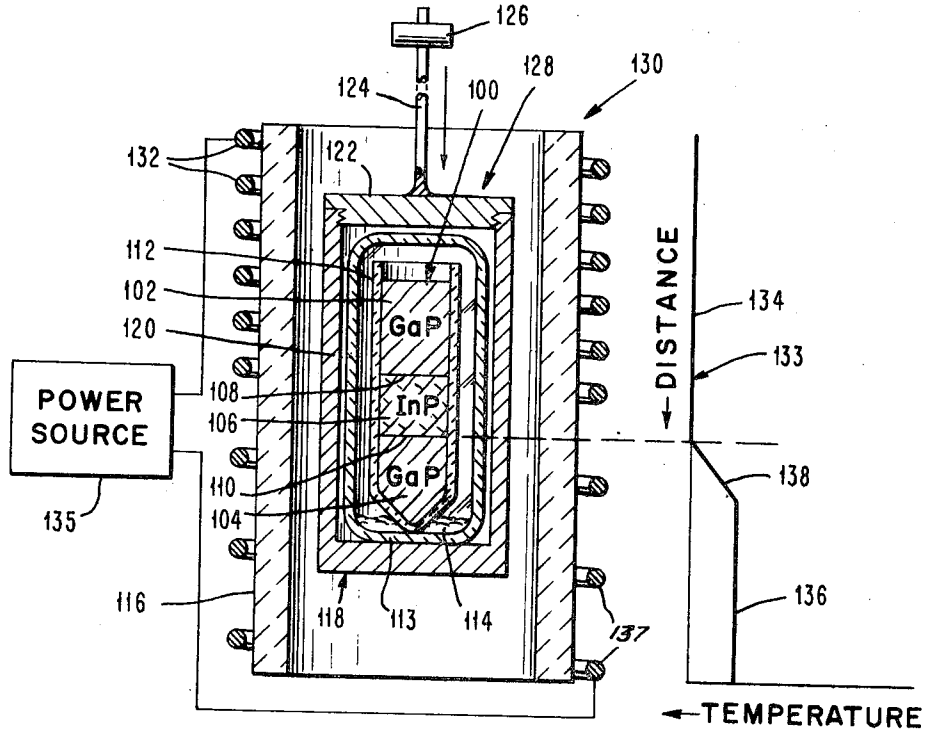


FIG. 1

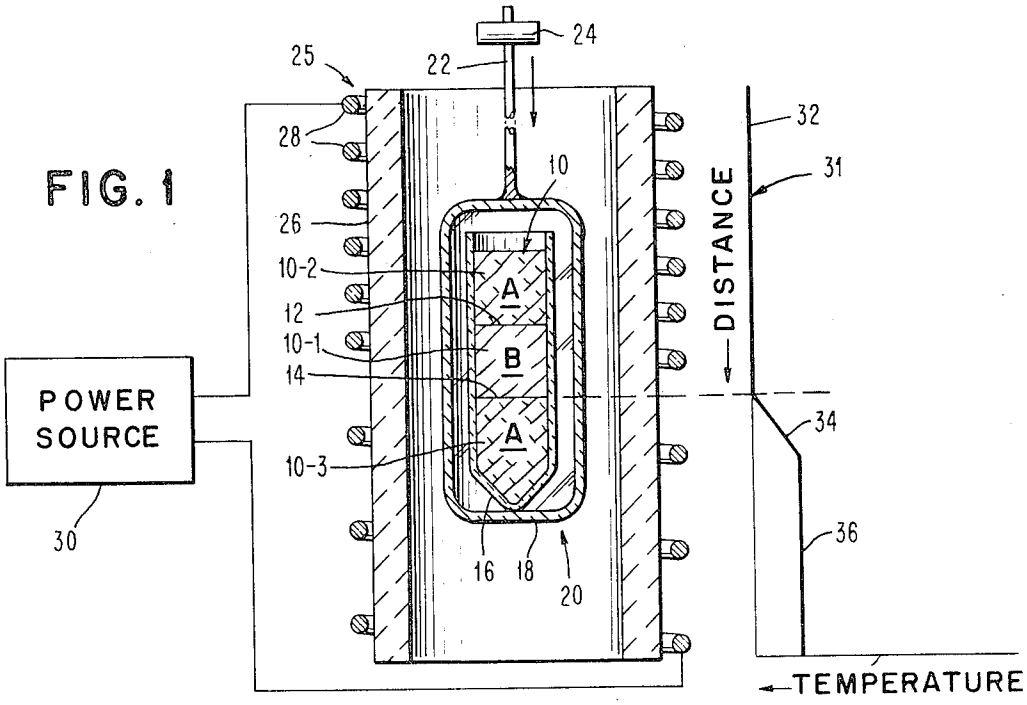
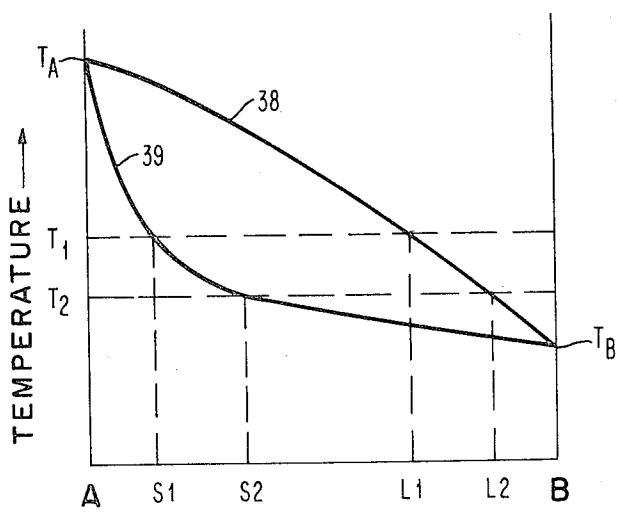


FIG. 2



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FIG. 3

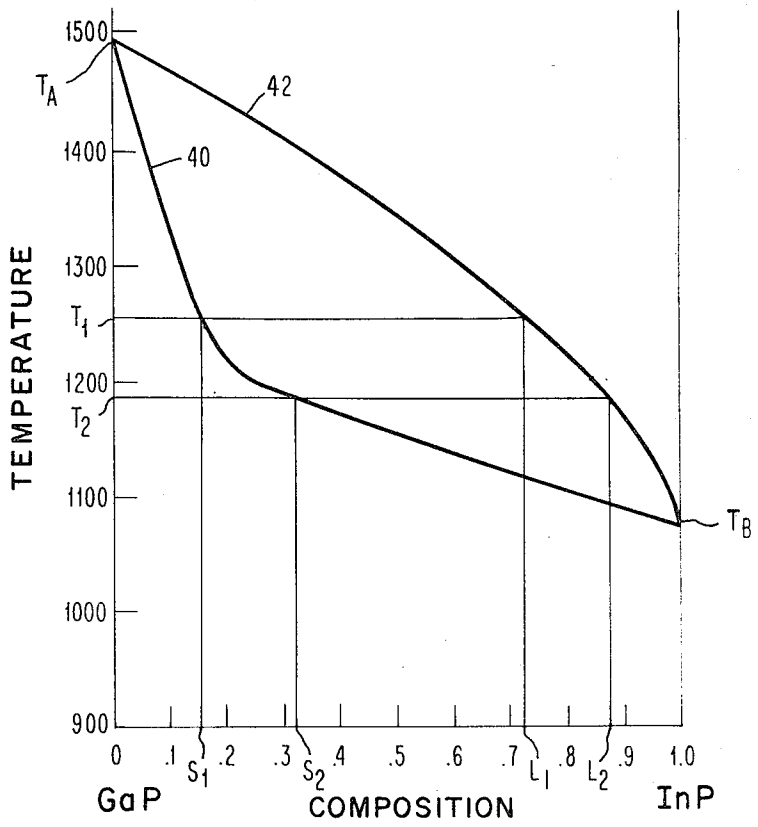

1500
T_A
42
1400
40
1300
T_1
1200
T_2
1100
1000
900
TEMPERATURE
T_B
0 .1 S_1 .2 .3 S_2 .4 .5 .6 .7 L_1 .8 L_2 .9 1.0
GaP
COMPOSITION
InP

FIG. 4

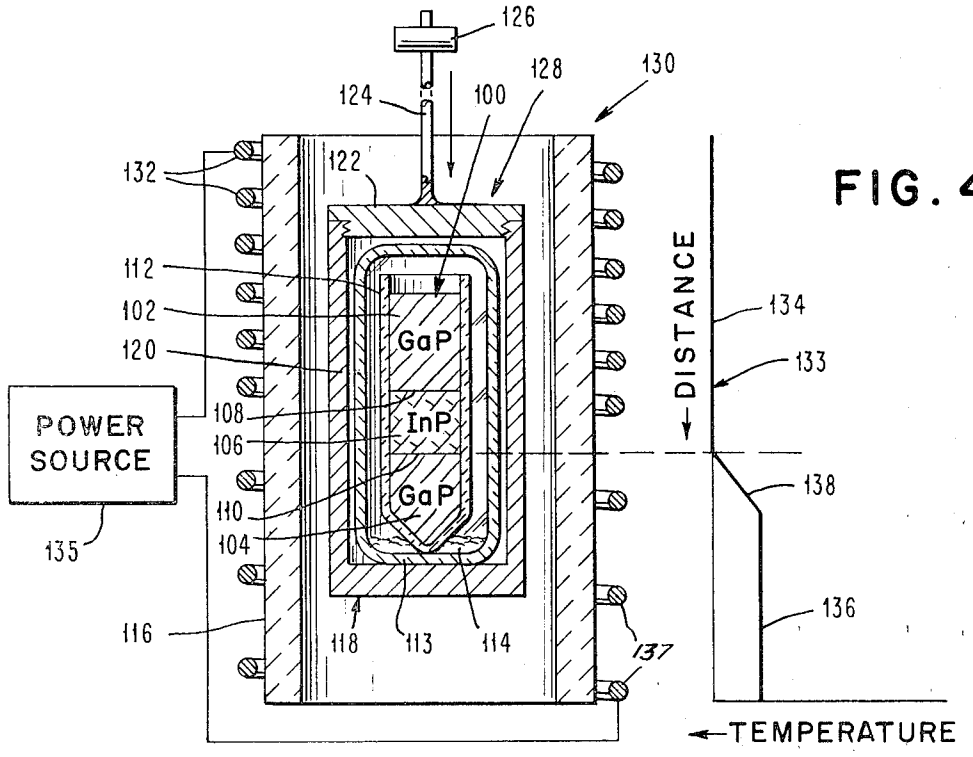

126
124
100
128
130
122
132
112
102
120
108
106
110
104
116
118
113
114
137
GaP
InP
GaP
POWER SOURCE
135
DISTANCE
134
133
138
136
TEMPERATURE

FIG. 5A

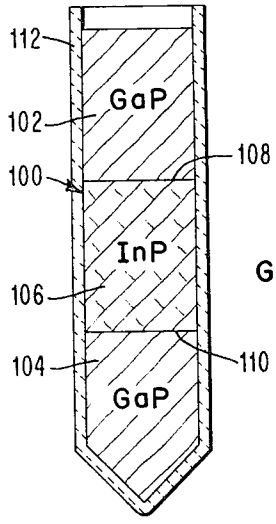


FIG. 5B

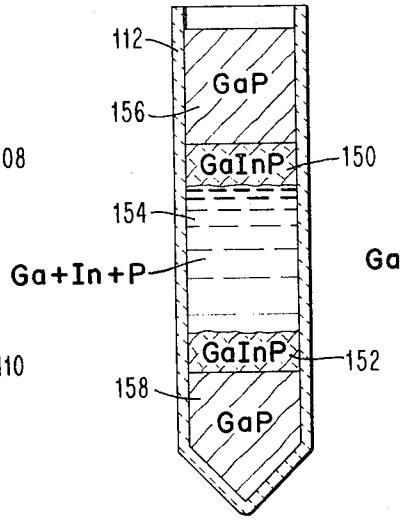
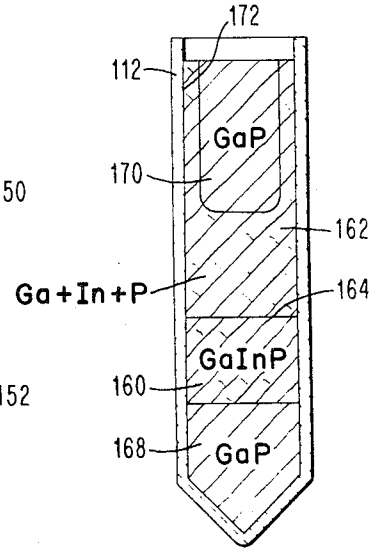


FIG. 5C



METHOD FOR GROWTH OF A MIXED CRYSTAL WITH CONTROLLED COMPOSITION

BACKGROUND OF THE INVENTION

This invention relates generally to growth of a mixed crystal of controlled composition and it relates more particularly to growth from a plurality of III–V compounds of a mixed crystal of relatively extensive dimensions of either homogeneous composition or variable composition in the growth direction.

Illustratively, mixed crystals are of interest for large direct band gap semiconductors, e.g., for electroluminescent diodes, and for semiconductor devices which require layers of alternating compositions, e.g., for bulk semiconductor oscillators. It has been difficult to grow large semiconductor mixed crystals of controlled compositions in the growth direction.

In the prior art, mixed crystals of two III–V compounds have been prepared by the solidification of a melt consisting of the III–V compounds with a range of composition dependent upon the shape of the solidus curve of the phase diagram. Generally, for many of the mixed III–V crystals of interest for semiconductor device technology, the mixed crystals crystallize in a region of the solidus which is appreciably flat and is appreciably distant from the liquidus on the composition scale of the phase diagram. Illustrative mixed-crystal systems with phase diagrams of this character are GaP-InP, Si-Ge, GaSb-InSb, and GaP-InAs. Conventional techniques for growth of mixed crystals by crystallization usually result in solids with rapidly varying or inhomogeneous composition in the growth direction which often limits their usefulness for both device technology and study purpose.

Heretofore, solid solution alloy crystals and mixed alloy crystals with homogeneous composition in the growth direction have been difficult to prepare. The equilibrium structure depends on composition as well as temperature and pressure. The limits or extent of existence of a particular structure for a constant pressure is representable on a diagram in which temperature and composition are different variables.

The equilibrium structure can be illustrated as a function of temperature and composition via a "phase diagram" or "equilibrium diagram." The actual growth of a solid from a liquid solution of two discrete components can be described with the use of a binary phase diagram or a pseudobinary diagram, i.e., isomorphic cut of a ternary diagram, where there is a continuous range of solid solutions. For a phase diagram illustrating the equilibrium cooling of an alloy or mixed alloy where A and B represent pure elements and/or compounds, A and B are generally referred to as the components of the system. Generally, an alloy of given composition exists as a single liquid solution of A and B at a temperature above the liquidus temperature for this composition. If heat is extracted from the alloy system, solidification begins at that temperature. The solidus line gives the composition of solid solution in equilibrium with the liquid solution. The composition of the incipient solid formed is given by the intersection of the temperature horizontal line with the solidus line. As heat is further extracted from the alloy system, the temperature is lowered and the liquid shifts its composition along the liquidus line to become more and more B-rich because of the rejection of B, e.g., growth of the A-rich solid at a nucleation site. Each new increment of solid forms with the appropriate equilibrium composition given by the solidus at the temperature of formation. The composition of the newly formed solid adjusts to each new equilibrium value by exchange of A and B atoms across the solid-liquid interfaces of the system. At any lower temperature than the initially given temperature, all the liquid has another composition and the solid formed has a new composition. The physical mechanism continues until solidification is complete at a final still lower temperature where the composition of the solid is equal to that of the alloy. Subsequent extraction of heat from the alloy system causes lowering of the temperature without further phase changes, i.e., the alloy remains a single solid solution. Upon heating the sequence of events is reversed.

For pure components A and B, freezing and melting are constant temperature phenomena. However, solidification and melting in each two-component or pseudo two-component alloy takes place over a range of temperatures. Hence, the solidification of any alloy system yields a nonhomogeneous solid whose composition varies according to the equilibrium solidus line.

Prior art patents and copending applications representative of the state of the art of interest for the practice of this invention are as follows:

a. U.S. Pat. No. 2,739,088 issued Mar. 20, 1956 to W. G. Pfann for "Process for Controlling Solute Segregation by Zone-Melting";

b. U.S. Pat. No. 3,242,015 issued Mar. 22, 1966 to D. M. Harris for "Apparatus and Method for Producing Single Crystal Structures";

c. U.S. Pat. No. 3,243,267 issued Mar. 29, 1966 to W. W. Piper for "Growth of Single Crystals";

d. U.S. Pat. No. 3,261,722 issued July 19, 1966 to W. Keller et al. for "Process for Preparing Semiconductor Ingots within a Depression";

e. U.S. Pat. No. 3,366,454 issued Jan. 30, 1968 to O. G. Folberth et al. for "Method for the Production and Remelting of Compounds and Alloys";

g. U.S. Pat. No. 3,378,350 issued Apr. 16, 1968 to Hiromu Sasaki for "Method for Growing Single Crystals of Vanadium Dioxide";

g. Copending commonly assigned application Ser. No. 646,315, filed June 15, 1967 by H. Rupprecht et al. for "-Preparation of Semiconductor Ternary Compounds";

h. Copending commonly assigned application Ser. No. 787,452, filed Dec. 27, 1968 by M. R. Lorenz et al. for "-Microwave Oscillators Using Semiconductor Alloys";

i. Copending commonly assigned application Ser. No. 811,870, filed Apr. 1, 1969 by L. Esaki et al. for "Semiconductor Bulk Oscillator";

j. Copending commonly assigned application Ser. No. 811,871, filed Apr. 1, 1969 by L. Esaki et al. for "Semiconductor Device with Superlattice."

SUMMARY OF THE INVENTION

This invention provides a method for growing a crystalline region of a mixed crystal which is applicable to multicomponent systems for which there is some solubility over a range of compositions. The phase diagram for the multicomponent system should indicate some solubility in both the liquid and solid phases or regions in the phase diagram with these characteristics. Therefore, for the practice of this invention, there is a range of mutual solid solubilities for the components of the multicomponent system. Illustratively, multicomponent systems are the mixed-crystal systems GaP-InP and GaSb-InSb.

Theoretically, a solid of one fixed composition will be in equilibrium or steady-state condition with a liquid of another fixed composition if all other conditions are maintained constant for a sufficient length of time. The preparation of a crystalline region of the desired mixed crystal is obtained in the practice of this invention by sandwiching an ingot of the lower melting temperature component between two layers of the higher melting temperature component to fabricate a charge. The charge is then established in equilibrium at a temperature above the lower melting temperature. An apparatus useful for the practice of the invention consists of an isothermal zone in a furnace of length comparable to the size of the desired region of the mixed crystal. There is a slight temperature differential toward lower temperature at one liquidus-solidus interface and a mechanical device for transporting the latter interface through the temperature differential or kink.

Generally, for providing a crystalline region of a mixed-crystal system by the practice of this invention, there is available a seed crystal of one of the components or constituents and single-crystal overgrowth is obtained from the melt of par-

ticular composition onto the seed. The use of heteronucleation is also included in the practice of this invention where the nucleation site may be an inert material such as quartz. Polycrystalline growth then usually results with controlled or homogeneous composition. However, the seed for starting the growth of the crystalline region can be another material which is both nonreactive and insoluble in the melt, e.g., sapphire for $Ga_xIn_{1-}P$, upon which single crystal growth of the mixed crystal can be obtained.

A system for the practice of this invention is not limited to only two components, e.g., a ternary system for which ternary solids are obtained from a ternary liquid is suitable for the practice of this invention. Further, composites with multiple layers are useful for the practice of this invention. As each successive layer is dissolved a different equilibrium is established so that crystalline growth is achieved which has zones of different compositions in the growth direction each being of homogeneous composition for the equilibrium of the particular temperature at which it equilibriates in the liquid phase.

It is an object of this invention to provide a method for growing a crystalline region of mixed crystal with a given composition profile in the growth direction of a mixed-crystal system with some solubility of the components in some physical state.

It is another object of this invention to provide a method for growing a crystalline region of a mixed crystal with a controlled composition in the growth direction for a mixed-crystal system wherein there is a range of compositions with at least some solubility in both the liquid and solid phases.

It is another object of this invention to produce a relatively large crystalline region of a binary or pseudobinary crystal system with substantially homogeneous composition of either polycrystalline structure or single-crystalline structure.

It is another object of this invention to provide a method for growing a single crystal of a mixed-crystal system for which there is a range of compositions, for which there is complete solubility in both the liquid and solid phases and for which there is a relatively wide separation in composition between the liquidus and solidus boundaries of the phase diagram for the system.

BRIEF DESCRIPTION OF THE DRAWINGS

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

FIG. 1 is a sectional view in elevation showing diagrammatically, apparatus for growing a crystalline region of a mixed-crystal system showing that initially a lower melting component is initially established as a layer between two layers of a higher melting component of which the lower one becomes the seed crystal for growth of the mixed crystal as the lower solid-liquid interface of the charge in equilibrium is lowered through a temperature kink.

FIG. 2 is an illustrative phase diagram for a pseudobinary mixed-crystal system useful for explaining the hypothesized physical mechanism by which a mixed crystal is grown in the practice of this invention.

FIG. 3 is a phase diagram for the $Ga_xIn_{1-x}P$ mixed-crystal system useful for explaining in detail the hypothesized physical mechanism for growth of a crystalline region from a liquid zone in the practice of this invention.

FIG. 4 is a cross-sectional view of apparatus for growing a mixed crystal of $Ga_xIn_{1-x}P$ from a composite structure of a layer of InP between layers of GaP in the presence of an overpressure of phosphorus vapor in the practice of this invention.

FIG. 5 presents three schematic views of the charge or composite showing the changes which take place therein during growth of a mixed crystal in the practice of this invention in which

FIG. 5A illustrates the initial condition wherein a layer of InP is established in a composite sandwich structure between layers of GaP.

FIG. 5B illustrates a later condition after the charge is held at a given temperature for a suitable period wherein the intermediate region has become essentially an equilibrium liquid solution containing Ga, In and P and relatively thin layers of Ga, In and P of solid are shown at the liquid-solid interfaces; and

FIG. 5C presents a characteristic autoradiograph of the $Ga_xIn_{1-}P$ mixed crystal grown by the practice of this invention and the rest of the original charge volume showing the various metallurgical aspects thereof.

PREFERRED EMBODIMENTS OF THE INVENTION

The preparation of an illustrative mixed crystal of fixed or homogeneous composition from the melt by the practice of this invention will now be described with reference to the schematic diagrams of FIGS. 1 and 2 which present a crystal growth arrangement showing the temperature profile of the furnace, and a phase diagram, respectively. Illustratively, the starting materials are pure III–V compounds, e.g., GaSb and IbSb, generally characterized as A and B. The practice of this invention will be described hereinafter in greater detail with reference to FIGS. 3 to 5 relating to crystal growth of the GaP-InP mixed-crystal system.

In FIG. 1, there is shown a three-layered composite or charge **10** comprising an ingot **10-1** of the lower melting III–V compound B which is flanked on both the top surface **12** and on the bottom surface **14** by layers **10-2** and **1-3**, respectively, of the higher melting compound A. The charge **10** is established in a boron nitride crucible **16** and sealed in vacuum in a quartz ampul **18** to establish assembly **20**. The assembly **20** is supported by rod **22** which can be raised or lowered by mechanical device **24** thereby raising or lowering assembly **20** in the furnace **25**. Furnace **25** comprises a furnace tube **26** upon which are wound heating elements **28** to provide the temperature profile **31** with upper isothermal region **32**, temperature differential **34** and lower isothermal region **36**. Heating elements are energized by power source **30**. The assembly **20** is allowed to equilibrate isothermally at a given temperature, e.g., T_1 of FIG. **2**, that will yield a liquid solution from which the resultant mixed crystal or mixed solid solution can crystallize. The location of the assembly **20** of FIG. **1** is shown already moved through the temperature kink **34**. Thereafter, the assembly **20** is slowly lowered into a slightly cooler zone in furnace **26**. Crystallization of the mixed-crystal compound of the desired composition is then initiated at solid-liquid interface **14** on the seed provided by the substrate ingot **10-3**. Illustratively, a $In_xGa_{1-x}Sb$ ingot of about 1 cm. length × 1.5 cm. diameter is readily produced by the practice of the method of this invention, as described with reference to FIGS. **1** and **2** where component A is GaSb (melting point of approximately 770° C.) and component B is InSb (melting point of approximately 550° C.).

CONSIDERATIONS FOR THE INVENTION

It has been discovered for the practice of this invention how to grow a mixed crystal with given mole fraction. In the practice of this invention, at least two solid phases are established in equilibrium with a liquid phase at a given temperature. As the temperature of one of the solid phases is lowered, liquid freezes out to form the solid related to the composition of the liquid phase. The liquid phase becomes enriched in the rejected solvent and dissolves some of the other solid of composition A to reestablish equilibrium.

Generally, with reference to FIG. **2**, at a given temperature T1 for a given alloy system, there can be two phases in equilibrium according to the phase diagram, i.e., a solid of composition S1 and a liquid of composition L1, and the alloy system is essentially an equilibrium one. At some lower temperature T2 solid of composition S2 would be in equilibrium with liquid of composition L2.

In the practice of the method of this invention, a layered structure or charge is used consisting of a bottom single-crystal "seed" of the higher melting component, e.g., GaP; an intermediate layer of the lower melting component, e.g., InP; and a top layer of the higher melting component. At a temperature which is intermediate between the melting points of the two components, the center portion of the charge dissolves sufficient material from the end layers to form a liquid solution with composition corresponding to the liquidus at that temperature. After the steady-state condition of the assembly, i.e., the charge and the container arrangement therefor, is attained, growth of the solid mixed crystal onto the seed end layer and the replenishment of the depleted higher melting component by dissolution at the top end layer is achieved by slowly lowering the assembly through a temperature gradient. The liquid zone is gradually consumed since the lower melting component is not replaced.

A phase diagram is a thermodynamic equilibrium diagram and represents a theoretical or ideal state for a given temperature and a given composition. In FIG. 2, the equilibrium liquids are given by the liquidus line 38 and the equilibrium solids are given by the solidus line 39. Basically, the practice of this invention during the solidification relates to change-of-state phenomena, from liquid to a solid. A higher order system than binary or pseudobinary is suitable for the practice of this invention, e.g., three components, or when each component is in the thermodynamic phase rule sense destined to form a stable equilibrium solid-phase composition at that temperature with the phase of the liquid composition.

Because at equilibrium, solidification is an infinite process, the solid composition grows very near equilibrium at all times. The crystals are grown at relatively rapid rates of several millimeters a day compared to growth rates obtained by prior art procedures. Illustratively, crystals are readily grown in 2 weeks whereas other known procedures require months for growth of a centimeter of crystal.

Qualitatively, the ultimate mixed crystal is synthesized from the components of the crystal. A presynthesis as required for other known procedures is not necessary. There is a minimum of control of parameters; by controlling one isothermal temperature, a melt is obtained from which a solid is frozen slowly and the desired composition is obtained with nominally uniform composition throughout the resultant ingot of less than 5 percent variation.

In the practice of this invention it is physically possible to synthesize a solid from the pure components from a liquid whose composition yields the solid with the desired composition upon solidification or freezing. As some solid freezes, an additional amount of the depleted component is provided at another location to maintain the steady-state composition of the liquid. There is obtained a homogeneous or constant composition crystalline layer in the growth direction growing onto the seed crystal.

For a charge comprising a layer 10–1 of compound B sandwiched between two layers 10–2 and 10–3 of compound A, where A has a higher melting temperature, as shown in FIG. 1, if temperature of the entire assembly or ensemble is raised, referring now to the phase diagram of FIG. 2, when the temperature of the ensemble reaches T_B which is the melting point of B, the intermediate layer 10–1 will melt. If the temperature is elevated higher than the temperature T_B, the equilibrium composition of the melt given by the phase diagram at Tl must achieve the composition L1. The layer 10–1 of B has the capacity to dissolve into it some of the layers 10–2 and 10–3 of A and form a liquid. If the temperature is fixed at T1 the composition of the liquid will become L1. If the temperature is kept isothermal, some B will diffuse in at each interface slightly into solid A to form a solid thin layer of indefinite thickness. At each interface between each layer of A and the newly established melt is a thin layer of solid S1. Then there is a region of molten A+B. The charge 10 is held isothermally until equilibrium is achieved, which may take some hours or a few days. If a driving force is imposed by lowering the ensemble 20 into a cooler zone at a slight temperature gradient 34, according to the phase diagram of FIG. 2, there will be lowering of the temperature of the melt and out of this now saturated solution will form a solid of composition S1. Because composition S1 is richer in A than the melt, the melt becomes depleted in A and is undersaturated with respect to A. However, there is a source of A at the top ingot, and additional A dissolves therefrom and the liquid will tend to go back toward the constant composition L1.

As the assembly 20 is lowered through the temperature gradient 34, more and more solid S1 crystallizes out onto the lower seed crystal A and more and more A from the top layer goes into the liquid solution to replenish it. This physical mechanism continues until all the A is depleted from the top layer or all the B in the liquid zone is depleted. Whichever one is depleted first terminates the reaction. Until that time, a homogeneous crystallization is obtained. It is believed that the differential temperature imposed on the system by dropping the charge out of the isothermal zone 32 is the driving force behind this crystal growth, and that the rate-limiting step in the process is the dissolution of A into the liquid zone. The rate at which the assembly is lowered through the temperature gradient 34 must be sufficiently slow so that the liquid phase can maintain essentially a steady-state concentration given by the point L1 in FIG. 2, for the isothermal temperature T1, i.e., temperature 32 of FIG. 1.

In the practice of this invention, a solid region or zone is obtainable with a desired graded range of compositions of a mixed-crystal system. This can be achieved by first equilibrating the three-layered structure 10 at a temperature 32 which will yield the desired starting solid composition. As the assembly 20 is lowered through the temperature differential 34, by slowly changing the equilibrium temperature 32, the crystallization of the solid zone of the mixed-crystal system is obtained of the desired compositional gradient.

In the practice of this invention, simultaneous growth of several solid zones of a mixed crystal system is obtainable, each being of different but homogeneous composition. This can be obtained by equilibrating several sequential three-layer composites or charges 10 in the same tube, not shown, with each composite being equilibrated at a different temperature 32. There is a comparable series of temperature differentials 34. Essentially, the lower temperature zone 36 is effectively the next upper temperature zone for the next solid zone to be grown.

EXAMPLES OF THE INVENTION

The growth of mixed crystals of the GaP-InP mixed-crystal system will now be described with reference particularly to FIGS. 3 to 5.

A phase diagram for the GaP-InP pseudobinary system for the practice of this invention is presented in FIG. 3. The solidus line 40 was obtained by chemically analyzing ingots grown at a specific temperature. Since the area of major interest for electroluminescent devices is approximately in the region of $In_{0.4}Ga_{0.6}P$ to $In_{0.1}Ga_{0.9}P$, the data points were taken in this region. The remaining shape of the curve was obtained by extrapolation to the melting points of the pure components. The liquidus line 42 was calculated by using an ideal liquid model for the solution of GaP and InP.

FIG. 4 shows an arrangement for growing a mixed crystal of $Ga_xIn_{1-x}P$ from a charge 100 consisting of upper and lower layers 102 and 104 of GaP between which there is sandwiched intermediate layer 106 of InP. An upper solid liquid interface 108 and a lower solid-liquid interface 110, respectively, are established between the layers 102 and 106 and between the layers 106 and 104. Charge 100 is established in boron nitride crucible 112 which is established in sealed quartz ampul 113 in vacuum.

For the GaP-InP-GaP charge 100, it is necessary, for single-crystal growth, that the liquid phase be a stoichiometry, the phosphorus pressure in the system must be equal to or greater than the phosphorus dissociation pressure of the melt. This

can be accomplished by the addition of excess phosphorus **114** in the bottom of quartz ampul **113**. Alternatively, a conventional two-zone furnace, not shown, can be used with condensed phosphorus at the cool end thereof. The temperature of the condensed phosphorus is controlled to achieve the desired pressure in the system. Because of the overpressure of phosphorus **114**, quartz ampul **113** is established in stronger graphite container **118** which has main shell **120** and screwcap **122**. Graphite container **118** is supported by rod **124** held by mechanism **126** for raising and lowering the assembly or ensemble **128** consisting of the graphite container **118** and its contents. Furnace tube **116** has upper heating windings **132** and lower heating windings **137** for establishing the temperature profile **133** with upper and lower isothermal zones **134** and **136** between which there is temperature differential or kink **138**. Windings **132** and **137** are energized by power source **135**. It has been determined for the practice of this invention that rates of growth of 0.1 to 0.5 cm. per day are obtainable for growth of single crystals of $Ga_xIn_{1-x}P$ of the mixed-crystal system GaInP. A suitable rate of growth is readily determined experimentally for the practice of this invention and is generally approximately inversely proportional to the equilibrium temperature of the liquid solution.

The InP layer **106** melts when the isothermal temperature **134** is higher than the melting point thereof and dissolves some of the GaP from both layers **102** and **104**. The maximum solubility is determined by the temperature **134** selected. A solid phase appears which is the equilibrium solid phase at the temperature T. This solid phase will be at both upper and lower liquid-solid interfaces **108** and **110**. The lower solid layer **104** of GaP of the composite or charge **100** is now cooled by lowering the assembly **128** through the temperature kink **138**, and a solid solution of constant composition precipitates or grows from the liquid at the expense of the upper solid layer **102** of GaP. The starting materials for an exemplary single crystal of GaP by the practice of this invention are:

GaP seed crystal **104** of 26.7 g. and length = 35.5 mm.,
InP layer **108** of 41.7 g. and length = 48.5 mm.,
GaP feed crystal **102** of 41.1 g. and length = 55.0 mm.,
P **114** of 6.5 g.

Illustratively, single-crystal overgrowth of a mixed crystal of $Ga_xIn_{1-}P$, according to the practice of this invention, has been realized in the GaP-InP system. The character of the crystalline growth has been determined by the use of radioactive InP.

FIGS. 5A, 5B and 5C illustrate on the same dimensional scale, three sequential stages of the growth of single crystal $Ga_xIn_{1-}P$. FIG. 5A shows the initial charge **100**; FIG. 5B shows the essentially equilibrium stage after the charge has been held isothermal for a suitable interval at temperature **134** of FIG. **4**, and FIG. 5C is a replica of an autoradiograph after this single crystal of $Ga_xIn_{1-x}P$ has been grown.

The nature of FIG. 5A has been described in detail above with reference to FIGS. **3** and **4**. In FIGS. 5B after equilibrium essentially has been attained at temperature **134**, the upper and lower solid-liquid interface regions **150** and **152** of GaP-InP are shown between the liquid region **154** of Ga+In+P and the upper and lower resultant solid regions **156** and **158**.

Finally, in FIG. 5C there is presented after a single crystal **160** of $Ga_xIn_{1-x}P$ has been grown, a replica of an autoradiograph after the entire assembly has been cooled to room temperature, e.g., 20° C. The remaining liquid solution **162** of Ga+In+P has solidified above the upper interface **164** of single crystal **160** of $Ga_xIn_{1-x}P$. There remain of the original layers **102** and **104** of GaP the lower region **168** and upper region **170**. In order that contact of the upper region **170** always be achieved with the liquid region **154** (FIG. 5B), it has a sufficiently large spacing from the wall **172** of the crucible **112** so that the liquid **162** has risen by capillary action along the sides thereof toward the top of crucible **112** and thereafter participated in dissolving the additional GaP sequenced for growth of single crystal **160**.

Illustratively, the region **160** of regrown single crystal Ga_x-$In_{1-x}P$ is an ingot of approximately 1 cm. length and 1.5 cm. diameter. The composition of the single crystal **160** as determined by conventional radiochemical procedure was $Ga_{0.72}In_{0.18}P$. The constancy of this composition was ±5 percent, i.e., In=0.18±0.01 and Ga=0.72±0.01.

We claim:

1. A method for growing a crystalline region of a mixed-crystal system with substantially homogeneous composition in the growth direction by the steps of:
establishing a substantially equilibrium liquid region for said composition;
establishing a first solid region of one component of said mixed-crystal system in contact with said liquid region at one temperature and a second solid region of said one component in contact with said liquid region at another location at another temperature; and
controlling the temperatures at said first and second locations for dissolving one solid component and depositing said crystalline region with said homogeneous composition at said other location.

2. A method for growing a crystalline region of mixed-crystal system of substantially homogeneous composition in the growth direction by the steps of:
establishing a first solid-liquid interface at one location adjacent a substantially equilibrium liquid zone for said composition;
establishing a second solid-liquid interface at another location adjacent said liquid zone;
controlling a temperature differential between said first and second locations for respectively
dissolving said first solid into said liquid zone at said first solid-liquid interface, and
depositing said crystalline region of said substantially homogeneous composition at said second solid-liquid interface.

3. A method for growing a crystalline region of a mixed-crystal system with substantially homogeneous composition in the growth direction by the steps of:
establishing a charge having first, second and third solid layers,
said first layer being of one component of said mixed-crystal system, and
said second and third layers being of another component of said mixed-crystal system,
said first layer being intermediate said second and third layers, and having lower melting point and complete solubility therewith over a range of compositions;
establishing a substantially equilibrium condition of said charge at a temperature above the melting point of said intermediate layer and below the melting point of said second and third layers to obtain a liquid zone with a given composition with first and second liquid-solid interfaces in said second and third solid layers;
lowering the temperature at one said solid-liquid interface between said intermediate liquid zone and one said adjacent solid layer; and
growing said crystalline region at said latter liquid-solid interface.

4. A method as set forth in claim 3 wherein said crystalline region is grown epitaxially.

5. A method as set forth in claim 4 wherein said crystalline region is single crystalline.

6. A method as set forth in claim 3 wherein said mixed-crystal system is a III–V semiconductor.

7. A method as set forth in claim 4 wherein said mixed-crystal system is GaP-InP, said composition is $Ga_xIn_{1-x}P$, said one component being InP and said another component being GaP.

8. A method for growing a single crystal with substantially homogeneous composition in the growth direction of a mixed-crystal system with at least two components and with a range of complete solubility in both the liquid phase and the solid phase by the steps of:

establishing a charge consisting of a solid region of one component of said mixed-crystal system with a relatively low melting point adjacent to at least one separated solid region of another component of said mixed-crystal system with a relatively high melting point;

heating said charge at a given temperature higher than said relatively low melting point but lower than said relatively high melting point for sufficient time to establish equilibrium of a resultant liquid region with said one solid region so that there is a percentage composition in said liquid region of each of said components of said mixed-crystal system according to the equilibrium solubilities at said given temperature; and

lowering the temperature at a location other than said one solid-liquid interface and growing thereat said single crystal.

9. A method for growing a solid region of a mixed-crystal system with controlled composition in the growth direction by the steps of:

establishing a substantially equilibrium liquid region for said composition;

establishing a first solid region of one component of said mixed-crystal system in contact with said liquid region at one temperature and a second solid region of said one component in contact with said liquid region at another location at another temperature; and

controlling the temperatures at said first and second locations for dissolving one solid component and depositing said solid region with said controlled composition at said other location.

10. A method as set forth in claim **9** wherein said controlled composition of said solid region includes a plurality of discrete layers with different compositions in the growth direction.

11. A method as set forth in claim **9** wherein said controlled composition is continuously variable in the growth direction.

12. A method for growing a solid zone with controlled composition in the growth direction of a mixed-crystal system with at least two components and with a range of complete solubility in both the liquid phase and the solid phase by the steps of:

establishing a charge consisting of a solid region of one component of said mixed-crystal system with a relatively low melting point adjacent to at least one separated solid region of another component of said mixed-crystal system with a relatively high melting point;

heating said charge at a given temperature higher than said relatively low melting point but lower than said relatively high melting point for sufficient time to establish equilibrium of a resultant liquid phase region with said one solid region so that there is a percentage composition in said liquid region of each of said components of said mixed-crystal system according to the equilibrium solubilities at said given temperature; and

lowering the temperature at a location other than said one solid-liquid interface and growing thereat said solid zone.

13. A method as set forth in claim **12** wherein said solid zone is crystalline.

14. A method as set forth in claim **13** wherein said solid zone is single crystalline.

15. A method as set forth in claim **12** wherein said solid zone has homogeneous composition in the growth direction.

16. A method as set forth in claim **12** wherein said solid zone includes a plurality of discrete layers with different compositions in the growth direction.

17. A method as set forth in claim **12** wherein said controlled composition of said solid zone is continuously variable in the growth direction.

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