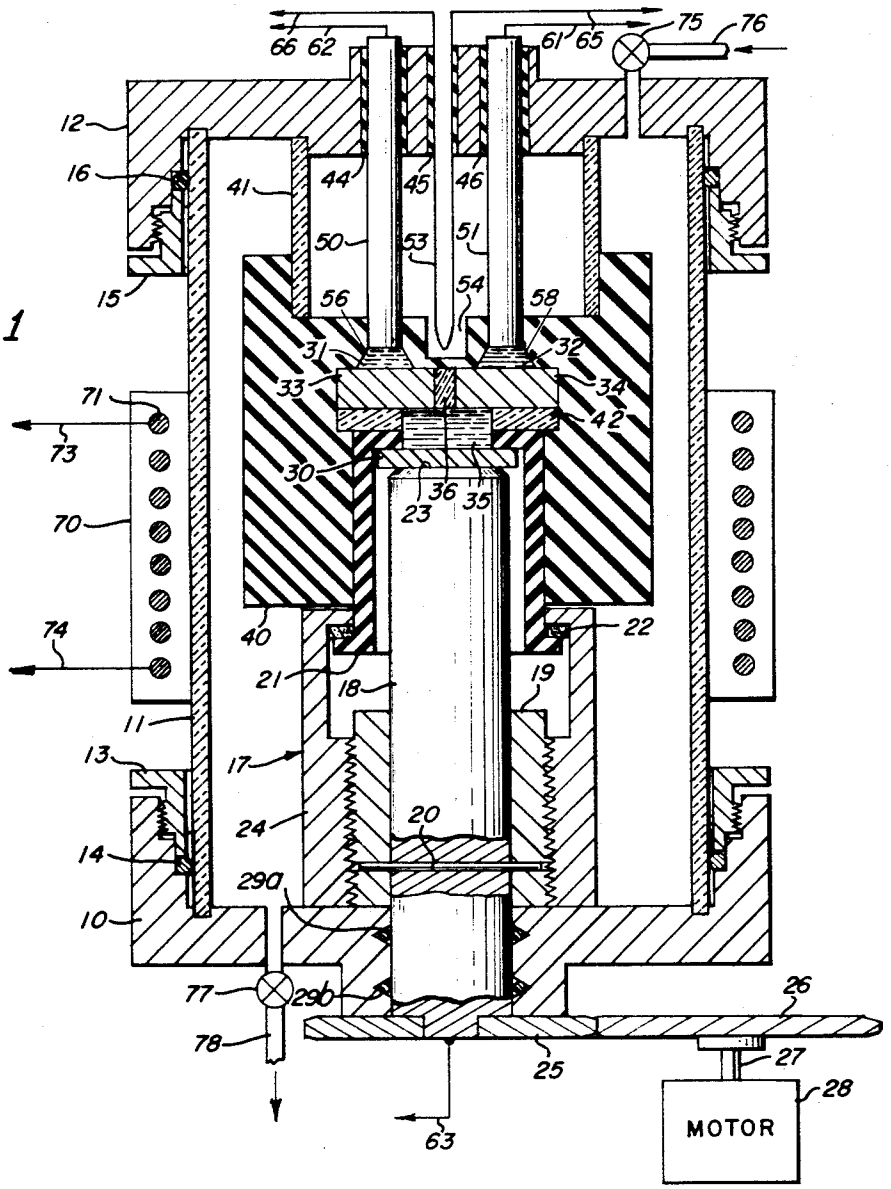
Nov. 19, 1968 R. F. TRAMPOSCH 3,411,946

PROCESS AND APPARATUS FOR PRODUCING AN INTERMETALLIC COMPOUND

Filed Sept. 5, 1963

FIG. 1



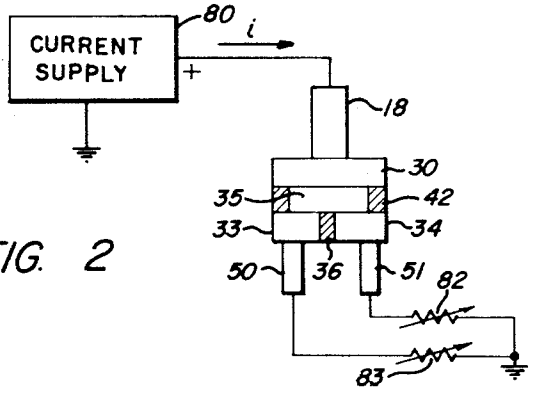


FIG. 2

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PROCESS AND APPARATUS FOR PRODUCING AN INTERMETALLIC COMPOUND

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This invention relates to semiconductor materials and more particularly to a thermoelectric technique for preparing semiconductor alloys from solution.

In the preparation of semiconductor alloys for use in transistors or lasers, it is desirable that alloy layers be of a controlled composition. Several attempts have been made in the past to obtain single crystal controlled alloy compositions, i.e., by promoting oriented growth of crystals upon a variety of single crystal substrate materials. A vapor evaporation technique was attempted many years ago, but the use of this technique has been limited due to the inability of producing uniform materials. Another method for growing semiconductor alloy layers by chemical decomposition from a vapor phase has been developed, but this technique although finding some success, is limited because of the difficulty of producing materials that are free of impurities.

Accordingly, it is the principal object of this invention to provide a new technique for preparing semiconductor alloys.

It is a further object to provide a nonvacuumized technique for growing semiconductor alloys.

It is an additional object to provide a technique utilizing thermoelectricity to produce a semiconductor alloy.

It is a further object to provide a nonvacuumized technique for growing alloys composed of volatile materials or elements.

It is another object of this invention to provide a three-element semiconductor alloy material which has a predetermined energy gap and dimensional spacing between atoms.

In accordance with the alloy preparation technique of this invention, compositions of semiconductor alloys are prepared by thermoelectrically controlling the amount of source material which is permitted to dissolve into and grow from a solution to form an alloy on a suitable substrate.

A source material is defined for purposes of this invention as that material which comprises at least one of the materials which constitutes at least a portion of the final composition of matter or alloy.

Other objects and features of this invention will become apparent from the following description taken in connection with the drawings, wherein:

FIG. 1 is a sectional view of an apparatus utilized in carrying out the principles of the present invention; and

FIG. 2 is a schematic diagram of the electrical portion of the apparatus which is used to control the composition of the alloy prepared in accordance with this invention.

Referring now to the drawing, and more particularly to FIG. 1 thereof, there is shown at **10** a bottom tube seat constructed of a bronze material. A top tube seat, also of bronze, is shown at **12**. Sealed between seats **10** and **12** is a quartz tube muffle **11**. Sealing of the seats and muffle is accomplished by the tightening of sealing jackets **13** and **15**, and the simultaneous forcing of O-rings **14** and **16** into contact with the muffle **11**. A rotatable assembly is shown at **17**. The assembly is supported by the bottom seat **10**. Assembly **17** comprises a graphite electrode **18** having mounted thereon an inner steel jacket secured by a steel pin **20**. An outer steel jacket **24** is

shown mounted on the inner jacket. The inner jacket is used to position a quartz crucible **21** above the electrode **18** in order to permit a seed or substrate **30** to be positioned on a top surface **23** of the electrode **18**. The substrate **30** is rigidly positioned between the electrode top surface **23** and the quartz crucible **21**. A thermoelectric expansion gasket **22** is mounted between crucible **21** and jacket **24**.

Graphite electrode **18** has a gear **25** mounted on one end to permit the assembly **17** to be rotated, thereby permitting the substrate **30** to rotate to obtain uniformity in crystal growth. A second gear **26** drives gear **25** by way of a shaft **27** which is coupled to a motor **28**. O-rings **29***a* and **29***b* seal the moving electrode **18** in the seat **10**.

A silicate housing **40** is shown mounted between the outer jacket **24** and the top seat **12** by a quartz insulator **41**. A quartz ring disc **42** cut out in the shape of a washer is shown positioned within the housing **40**, and on top of the crucible **21**. The disc **42** permits a portion of a solvent **35** to be held in position above the substrate **30**. A first source of material **33** and a second source of material **34** in the shape of half discs are mounted in contact with the solvent **35** interface. The materials **33** and **34** are separated by a quartz rectangularly shaped insulator **36**.

Three openings in top seat **12** are shown, each of which are lined with quartz insulating jackets **44**, **45** and **46**. A first electrode **50** passes through jacket **44** to enter a cavity **56** in housing **40**. A solvent **31** is used to make good electrical contact between the material **33** and the electrode **50**. A second electrode **51** passes through the jacket **46** to enter a cavity **58** in housing **40**. A solvent **32** is used to make electrical contact with source material **34**. A thermocouple **53** passes through the jacket **45** to enter a cavity **54** in housing **40**. Thermocouple **53** is used to measure the temperature in the vicinity of the materials **33**, **34** and substrate **30** during the alloy growing process. Electrical contacts are made to electrodes **18**, **50** and **51** by leads **63**, **62** and **61**, respectively. Leads **65** and **66** connect thermocouple **53** to external temperature metering devices.

A conventional resistance heating apparatus is shown at **70** having electrical leads **73** and **74**. The heating apparatus **70** is positioned around the muffle **11** in order to keep the materials **33**, **34**, solvent **35**, and substrate **30** at a proper system operating temperature so that rapid dissolution of materials **33** and **34** can take place, and further, to insure that the solvent remains in a liquid form. An intake gas tube **76** and valve **75** is mounted on top seat **12**. The valve is used to permit an inert gas to enter the apparatus. A second exhaust valve **77** and tube **78** is mounted on bottom seat **10** to permit a constant flow of the inert gas.

Referring to FIG. 2, there is disclosed a schematic diagram of a coupling arrangement to control thermoelectric heating of the materials **33** and **34** and the solvent **35**. A current supply **80** is shown providing a current *i* to electrode **18**. The flow of current is in a direction such that the current *i* enters electrode **18** and first travels through the substrate, then the solvent, and last through the source materials. This direction of current flow provides for cooling at the interface between the substrate and the solvent and heating at the interface of the solvent and the source materials. A variable resistor **82** is connected to electrode **51** to control the amount of current flowing through a path comprising substrate **30**, solvent **35**, and source material **34**. A second variable resistor **83** is connected to electrode **50** to control the amount of current flowing through a path comprising substrate **30**, solvent **35**, and source material **33**. By adjusting these resistors,

the composition of the alloy to be formed is controlled. Composition of the alloy is controlled by the current density which in turn determines the amount of materials **33** and **34** dissolved at the interface of the solvent **35** due to thermoelectric (Peltier effect) heating at a solid to liquid interface. It is to be noted that the material that dissolves enters the solvent solution and crystallizes onto the substrate due to cooling taking place at the interface between the liquid solvent **35** and the solid substrate **30**.

Referring once again to FIGS. 1 and 2, a description will be given for applying this invention to the preparation of a gallium arsenide phosphide alloy. By way of example, a single crystal of gallium arsenide oriented along its (111) crystallographic axis and having a surface area in the order of ½ square centimeter at its interface with a solvent **35**, is chosen as a suitable substrate **30** for the preparation of this alloy. A substrate comprised of at least a portion of the alloy to be formed is preferred in order to limit the possibility of impurities forming in the alloy to be grown upon a surface of the substrate. The crystallographic axis orientation is chosen in this instance to obtain a grown single crystal which will exhibit a (111) crystallographic axis orientation. Although this axis is chosen, it is to be understood that other orientations of crystal growth, for example, along the (101) axis, is obtainable by using a substrate oriented along its (101) crystallographic axis.

Gallium (Ga) is chosen as a solvent **35**, in this instance, since it is a liquid at the temperatures used in the preparation of the alloy. Furthermore, the use of a solvent comprised of one of the elemental materials of the alloy to be formed also prevents the possibility of impurities entering the alloy. Gallium is also chosen as solvents **31** and **32** in order to permit a good electrical contact to be made by the electrodes **50** and **51** and source materials **33** and **34**, respectively. The quartz disc of this invention, **42**, has a thickness dimension in the order of .020 inch and has a quartz-free area in the disk of approximately ½ square centimeters. The depth of the gallium solvent is slightly greater than .020 inch, which is the thickness dimension of the disc **42**. A first solid source material **33** of gallium arsenide (GaAs) is used as disc **33**. A second source material of gallium phosphide (GaP) also comprises material **34**. Each of the materials **33** and **34** has a surface area in contact with the solvent **35** in the order of between ⅛ square centimeter and ¼ square centimeter. An inert gas, such as 95% nitrogen and 5% hydrogen, is continuously pumped through the apparatus via intake valve **75** and exhaust valve **77**. The materials **33** and **34**, the solvent **35**, and the substrate **30** are heated by the resistance heating apparatus **70** to a temperature above 800° C. but below 1000° C. At these temperatures gallium **35**, **31** and **32** is in a liquid form and the substrate Ga As and the source materials Ga, As, and GaP are in a solid form. The substrate **30** is continuously rotated by motor **28** which in turn rotates the assembly **17**. This permits a homogeneous crystal growth to form at the interface between the solvent **35** and the substrate **30**.

The current *i* shown in FIG. 2 is permitted to flow into electrode **18**. This current *i* passes through the substrate **30**, the solvent **35**, and divides between the two source materials **33** and **34**. The division of the current *i* between the two source materials **33** and **34** is controlled by the variable resistors **82** and **83**, connected to electrodes **51** and **50**, respectively. By controlling the amount of current and the current density in this manner, the percentages of the chemicals As and P in the grown alloy can be controlled. Current densities in the order of 40 amps. per square meter were utilized in the preparation of gallium arsenide phosphide alloys. The flow of current *i* at the interface between the source materials **33** and **34**, and the solvent **35**, produces a thermoelectric heating effect or phenomena. This effect is generally known as the Peltier effect. The heating at the interface of the solvent and the sources of materials causes the materials to dissolve and saturate the solvent to a predetermined degree dependent upon the current density passing through each of the materials. The amount of current density, therefore, controls the dissolution rate of the alloy material components and consequently the composition of the grown alloy crystal layer. Growth on the substrate **30** takes place because of the thermoelectric phenomena, known as the Peltier effect, which causes cooling to take place at the interface of the liquid gallium **35** and the solid substrate **30**. This cooling causes crystallization of the materials which were previously dissolved into solvent.

Thus, a technique has been described for growing a gallium arsenide phosphide crystal alloy material which is today finding many uses in laser applications. The technique described herein permits the growth of semiconductor alloys having predetermined energy band gaps since the energy band gap is a function of the alloy composition of the material. Additionally, alloys having predetermined atomic dimensions between atoms can be grown. Materials having predetermined frequency characteristics can be obtained using the technique described herein. These materials are particularly suitable for use as crystals in laser applications. Furthermore, it is to be noted that strictly from an impurity standpoint, much higher purity alloys can be obtained by employing this method since only those elements which are involved in the preparation of the alloy material are present.

The technique of the present invention is also suitable for growing other alloys from a solid solution such as an indium arsenide phosphide alloy using an indium solvent and operating at a solution temperature of approximately 550° C. Another alloy material of a germanium gallium arsenide compositon could also be epitaxially grown using gallium as a solvent and operating at a temperature of approximately 550° C. Other alloys could comprise silicon gallium phosphide using gallium as a solvent and operating at a temperature of approximately 1000° C. and aluminum arsenide phosphide material using aluminum as a solvent. In additon, the technique of this invention is suitable for epitaxially growing two-element crystals by using a single source material of the crystal composition desired. By changing the crystallographic axis orientation of the substrate, a two-element crystal having any desired crystal lattice orientation can be obtained. This also holds true of three or more elemental crystal alloy structures. Accordingly, it is desired that this invention not be limited except as defined by the appended claims.

What is claimed is:

1. A nonvacuumized process for producing an intermetallic compound comprising passing a current flow through at least one source material capable of being dissolved and thereafter recrystallized, a solvent forming a solid to liquid interface with said material, and a substrate forming a liquid to solid interface with said solvent, said current producing a thermoelectric heating effect to dissolve said source material into said solvent at said solid to liquid interface and a thermoelectric cooling effect at a solvent substrate interface spaced from said solid to liquid interface to form an intermetallic compound coating on said substrate.

2. A nonvacuumized process for producing an intermetallic compound comprising passing a flow of current through at least two metallic source materials capable of being dissolved and thereafter recrystallized, a solvent forming a solid to liquid interface with both of said materials, and a substrate forming a liquid to solid interface with said solvent, said flow of current producing a thermoelectric heating effect to dissolve said source materials into said solvent at said liquid to solid interface and a thermoelectric cooling effect at a solvent substrate interface spaced from said solid to liquid interface to form an intermetallic compound coating of said substrate.

3. A process in accordance with claim **2** wherein said

solvent comprises an element found in at least one of said source materials.

4. A process in accordance with claim 2 including simultaneously heating said materials to a temperature above the melting point of said solvent.

5. A process in accordance with claim 2 including individually controlling the flow of current through each of said materials to control the percentage of each source material contained within the grown alloy.

6. A process in accordance with claim 2 wherein at least one of said source materials comprises a volatile substance.

7. A process for growing an intermetallic compound comprising passing a flow of current through a first layer comprising a first multi-element source material of GaAs and a second multi-element source material of GaP insulated from each other, a solvent layer forming a solid to liquid interface with said source materials, and a substrate layer forming a liquid to solid interface with said solvent, said current producing a thermoelectric heating effect to dissolve said source materials into said solvent at said solid to liquid interface and a thermoelectric cooling effect at a solvent substrate interface spaced from said solid to liquid interface to form an intermetallic compound coating of said substrate.

8. A process in accordance with claim 7 including an additional step of controlling the flow of current passing through each of said source materials to control the composition of said alloy.

9. A process in accordance with claim 7 wherein said solvent comprises Ga.

10. A process in accordance with claim 8 including an additional step of heating said materials, solvent and substrate to a temperature above the melting temperature of said solvent.

11. A process for producing an intermetallic compound comprising passing a flow of current through a combination of a first layer comprising a first multi-element source of InAs and a second multi-element source of InP insulated from each other, a solvent layer forming a solid to liquid interface with said source materials, and a substrate layer forming a liquid to solid interface with said solvent, said current producing a thermoelectric heating effect to dissolve said source materials into said solvent at said solid to liquid interface and a thermoelectric cooling effect at a solvent substrate interface spaced from said solid to liquid interface to form an intermetallic compound coating of said substrate.

12. A process in accordance with claim 11 wherein said solvent comprises In.

13. A process in accordance with claim 11 including an additional step of controlling the flow of current passing individually through each of said source materials to control the composition of said compound.

14. A process in accordance with claim 12 including an aditional step of heating said source materials, solvent and substrate to a temeperature above the melting temperature of said solvent.

15. A process for producing an intermetallic compound comprising passing a flow of current through a combination of a first layer comprising a source material of Ge and a multi-element source material of GeAs insulated from each other, a solvent layer forming a solid to liquid interface with said source materials, and a substrate layer forming a liquid to solid interface with said solvent, said current producing a thermoelectric heating effect to dissolve said source materials into said solvent at said solid to liquid interface and a thermoelectric cooling effect at a solvent substrate interface spaced from said solid to liquid interface to form an intermetallic compound coating of said substrate.

16. A process in accordance with claim 15 including an additional step of controlling the flow of current passing individually through each of said source materials to control the composition of said compound.

17. A process in accordance with claim 16 including an additional step of heating said materials, solvent and substrate to a temperature above the melting tmeperature of said solvent.

18. A process in accordance with claim 15 wherein said solvent comprises Ga.

19. A process for producing an intermetallic compound comprising passing a flow of current through a combination of a first layer comprising a first source material of Si and a multi-element source material of GaP insulated from each other, a solvent layer forming a solid to liquid interface with said source materials, and a substrate layer forming a liquid to solid interface with said solvent, said current producing a thermoelectric heating effect to dissolve said source materials into said solvent at said solid to liquid interface and a thermoelectric cooling effect at a solvent substrate interface spaced from said solid to liquid interface to form an intermetallic compound coating of said substrate.

20. A process in accordance with claim 19 including an additional step of controlling the flow of current passing individually through each of said source materials to control the composition of said alloy.

21. A process in accordance with claim 20 including an additional step of heating said materials, solvent and substrate to a temperature above the melting temperature of said solvent.

22. A process in accordance with claim 19 wherein said solvent comprises Ga.

23. A process for producing an intermetallic compound comprising passing a flow of current through a first layer comprising a multi-element source material of AlAs and a multi-element source material of AlP insulated from each other, a solvent layer forming a solid to liquid interface with said source materials, and a substrate layer forming a liquid to solid interface with said solvent, said current producing a thermoelectric heating effect to dissolve said source materials into said solvent at said solid to liquid interface and a thermoelectric cooling effect at a solvent substrate interface spaced from said solid to liquid interface to form an intermetallic compound coating of said substrate.

24. A process in accordance with claim 23 including an additional step of controlling the flow of current passing through each of said source materials to control the composition of said alloy.

25. A process in accordance with claim 24 including an additional step of heating said materials, solvent and substrate to a temperature above the melting temperature of said solvent.

26. A process in accordance with claim 23 wherein said solvent comprises Al.

27. A process for producing an intermetallic compound comprising providing a current flow through at least one source of material selected from the group consisting of Ge, Si, GaAs, GaP, InAs, InP, AlAs, and AlP, a solvent forming a solid to liquid interface with said source, said current producing a thermoelectric heating effect to dissolve said source material into said solvent at said solid to liquid interface and a thermoelectric cooling effect at a solvent substrate interface spaced from said solid to liquid interface to form an intermetallic compound coating of said substrate.

28. An apparatus for an intermetallic compound comprising means for placing at least one source material in contact with a solvent, means for placing a substrate in contract with said solvent, and means for providing a current flow through said source material, said solvent and said substrate to create a heating effect to dissolve said source material into said solvent at said solid to liquid interface and a thermoelectric cooling effect at a solvent substrate interface spaced from said solid to liquid inter-

face to form an intermetallic compound coating of said substrate.

29. An apparatus in accordance with claim **28** including means for heating said solvent to a temperature above its melting point.

30. An apparatus in accordance with claim **28** including means for rotating said substrate to obtain a homogeneous compound.

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