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Cincinnati, Ohio
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[54] **INFRARED DETECTING MATERIALS**
4 Claims, 3 Drawing Figs.

[52] U.S. Cl..... **29/194,**
148/1.6
 [51] Int. Cl..... **B32b 15/00**
 [50] Field of Search..... **29/194;**
148/1.6, 171; 75/134 T

[56] **References Cited**

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ABSTRACT: Infrared detector material is formed by the epitaxial growth of a single crystal alloy of the two III-V compounds InAs and InSb on an InAs substrate. In the method of such growth, a liquid solution is prepared with excess indium solvent, InSb, and sufficient InAs to saturate the indium at 500° C. The InAs substrate, oriented in the III direction is immersed in the solution, and the substrate and the solution are brought to equilibrium at approximately 500° C. Slowly lowering the solution temperature causes a single crystal to be epitaxially grown on the substrate as a solid homogeneous InAs-InSb solution. Composition of the crystal is a function of solution composition and may be controlled by dissolving selected quantities of InSb in the solution.

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INFRARED DETECTING MATERIALS

This is a division of application Ser. No. 734,715 filed June 5, 1968 now U.S. Pat. No. 3,558,373, dated Jan. 26, 1971.

BACKGROUND

Our invention relates to infrared detector materials involving semiconductor crystals, and more particularly relates to epitaxially grown single crystal alloys of III-V compounds. In this connection, it may be pointed out that by group III elements we mean aluminum, gallium and indium; and by group V elements, we mean phosphorous, arsenic, and antimony. Various compounds of group III and group V elements have been found to have properties which, for some applications, are superior to those of the group IV semiconductor materials. They offer a wider range of energy gaps. Several methods have become known for the preparation of various single III-V compound crystals. Homogeneous alloys by chemical vapor deposition have been made of certain gallium, aluminum, indium, phosphides and arsenides, but attempts to make other pseudobinary III-V alloys (e.g., InAs and InSb alloys) by chemical vapor deposition have not met with success.

After the investigation of III-V compounds was begun, it was suggested that alloys of these compounds could be made, thereby extending the range of properties of the III-V compounds. Of particular interest to us were alloys of indium arsenic and indium antimonide. These have been found to have an energy gap ranging from about 0.1 ev. or less to 0.45 ev., depending on composition and temperature, making them especially well suited for infrared detection.

At least three methods have been used to make alloys of InAs and InSb. These have usually resulted in polycrystalline alloys, or at best in nonhomogeneous single crystal alloys. The properties of InAs-InSb alloys have been determined from such polycrystalline or nonhomogeneous single crystal alloys. Although the art has for several years appreciated the desirability of single crystal homogeneous solid solutions of III-V compounds, and although several attempts have been made to produce such crystals, to our knowledge none of the attempts made prior to our invention have been successful.

The earliest attempt to produce homogeneous ingots was the annealing of fine compressed powders of InAs and InSb. Although this method did produce ingots with homogeneous regions, the ingot itself was not homogeneous. This method takes anywhere from several weeks to several months and results in polycrystalline ingots.

Zone recrystallization, similar to zone refining, has also been used. However, this method, while producing ingots with homogeneous regions, produces polycrystalline ingots.

Directional freezing has also been used, but it too produces polycrystalline ingots.

There is need for an infrared detector material utilizing a single crystal homogenous alloy of III-V compounds.

There is a need for a method which can be used to produce single crystal homogenous alloys of III-V compounds.

There is a need for a composition which can be used to produce single crystal homogenous alloys of III-V compounds.

It is therefore an object of our invention to provide infrared detector material utilizing a single crystal homogenous alloy of III-V compounds.

It is a further object of our invention to provide epitaxially grown homogeneous alloys of III-V compounds on a suitable substrate.

A further more specific object of our invention is to provide a method and a composition for the epitaxial growth of a solid homogeneous solution of InAs and InSb on a substrate of either InAs or InSb.

Further objects and features of our invention will be apparent from the following specification and claims when considered in connection with the accompanying drawings illustrating several embodiments of our invention.

SUMMARY OF THE INVENTION

The invention involves, in one aspect, a new infrared detector structure. In another aspect, it involves a method for producing a single crystal alloy of two III-V compounds, such as for example InAs and InSb, the method comprising: (a) melting the two III-V compounds and a suitable solvent, such as excess indium, in a crucible; (b) effecting the saturation of the solvent with one of the compounds, such as for example InAs; (c) immersing a suitable prepared substrate in the solution, the substrate comprising a crystal having a lattice structure and spacing similar to that of the III-V compounds dissolved in the solvent, such as for example an InAs substrate; (d) effecting growth of an alloy crystal on the substrate by lowering the temperature of the solution; (e) and removing the substrate and the grown alloy crystal from the solution; wherein said compounds crystallize on the substrate to form a single crystal with improved homogeneity.

The invention also involves a composition which is a solution for use in the epitaxial growth of crystals comprising: (a) a solvent such as, for example, indium; (b) a first III-V compound, such as for example InAs, dissolved in the solvent; and (c) a second III-V compound, such as for example InSb, dissolved in the solvent. The solution is particularly useful when an excess indium solvent is saturated in either the InAs or the InSb.

DESCRIPTION OF THE VIEWS

FIG. 1 is a view in front elevation of an apparatus useful with our invention to produce crystals, the apparatus being shown with a segment removed to expose, in vertical section, the inside of the apparatus;

FIG. 2 is a triangular coordinate diagram illustrating the composition of the solution used and the resulting crystal formed in several examples of our invention;

FIG. 3 is a triangular coordinate diagram illustrating similar data in several more examples of our invention.

In describing the preferred embodiment of the invention illustrated, specific terminology will be resorted to for the sake of clarity. However, it is not intended to be limited to the specific terms so selected, and it is to be understood that each specific term includes all technical equivalents which operate in a similar manner to accomplish a similar purpose.

DETAILED DESCRIPTION

Apparatus used by us is similar to a Czochralski crystal pulling apparatus and is illustrated in FIG. 1. Generally, it comprises a suitable cylindrical casing 10 with a sealable top 12. The casing has a pedestal 14 to support a graphite crucible 16.

A substrate holder 18, which can be a modified Czochralski pulling rod, extends through the top 12 and is longitudinally (i.e., vertically) movable. The rod, however, should not be a good heat conductor since we do not want heat loss through the rod. An RF or resistance heating coil 20 surrounds the casing 10 for heating the crucible and its contents.

Suitable temperature-sensing devices, such as thermocouple transducers, may be contained by two thermocouple tubes such as 22a and 22b. One such thermocouple tube 22a positioned within the substrate holder 18 is connected by a wire 24 to a temperature-indicating device (not shown) and senses the temperature of the crucible contents.

In general, our method begins by obtaining a solution of two selected III-V compounds preferably having a common group III element. This is done by dissolving the compounds in a suitable solvent which we prefer to be an excess of the common group III element. We prefer to dissolve a sufficient quantity of one of the III-V compounds so that we can saturate the solution in that compound at a selected equilibrium temperature. The quantity of the other III-V compound is selected in order to result in a desired crystal composition.

Thus the two III-V compounds are first melted together with the solvent to obtain the desired solution, and the solution is homogenized. A substrate is then immersed in the solution and equilibrated with it at an equilibrium temperature. The substrate should be a material which has the same lattice structure as each of the III-V compounds and as nearly as practical the same lattice spacing. We prefer to use a substrate of one of the two III-V compounds of the solution and in particular of the III-V compound in which the solution is saturated.

Such a substrate when immersed in and equilibrated with the solution provides a favorable site for precipitation. As the solution then is cooled, a single crystal alloy is epitaxially grown on the substrate. The composition of the epitaxial layer is a function of the solution composition. After growth, the substrate is withdrawn, treated, and tested in ways familiar to those skilled in the art.

We have found it desirable to "soak" the substrate in the solution at equilibrium prior to initiating growth. This is especially helpful when we plan to cool at a fast rate such as approximately 200° C. per hour. In such case, we have "soaked" the substrate for 2 hours before, and the substrate and grown crystal 2 hours after, growth.

To grow InAs-InSb alloy crystals according to the preferred embodiment of our invention, we first obtain a solution of InAs and InSb dissolved in indium. The solution is obtained by melting together suitable amounts of InAs, InSb and excess indium in the crucible 16. Heat is supplied from the heater 20. Of course, prior to melting, the substrate holder 18 is maintained out of the crucible 16 so that a suitably prepared substrate can be positioned in a lateral slot in the holder 18 at the raised position of 30a.

After the indium, InAs, and InSb are melted and the solution 32 in the crucible 16 is homogenized, the substrate holder 18 is lowered, and the substrate is immersed in the solution 32 at the lowered position of 30b. The substrate and the solution are equilibrated at a temperature which is between the melting point of indium (155° C.) and the melting point of the substrate which in the case of InAs is 942° C. and in the case of InSb is 525° C. We have at times used an equilibrium temperature of about 500° C. If the solution is saturated in InAs, we prefer to use an InAs substrate. As we cool the solution 32, a single crystal alloy of InAs and InSb is obtained on the substrate by epitaxial growth.

FIG. 2 and FIG. 3 illustrate the compositions of some of the specific examples we have performed and the crystals we have obtained. The coordinates are for mole percentages of indium, arsenic, and antimony. The lines 50 and 51 represent a range of liquid solution compositions, and the lines 52 and 53 represent the range of crystal compositions. In the examples illustrated in FIG. 2, the solutions were equilibrated at approximately 500° C. before cooling and crystal growth was begun. In the examples illustrated in FIG. 3, 400° C. was the approximate equilibrium temperature.

In performing the examples, the indium, indium arsenide, and indium antimonide used were substantially pure so that the compounds, substrate and alloy consisted essentially of the elements in the proportions and ranges specified. However, it is obvious that other proportions may be used and that additional impurities could be either unintentionally or intentionally introduced.

The following examples illustrate the process and the composition of the invention using particular materials, steps and conditions. It is to be understood that these examples are furnished by way of illustration and are not intended to be by way of limitation.

EXAMPLE I

Indium, InSb, and sufficient InAs to saturate about 20 grams of indium at 500° C. were melted together to obtain a solution, illustrated by the point 54 in FIG. 2, comprising in mole percentages-1,10 percent arsenic (1.36 percent InAs), 18.12 per-

cent antimony (22.44 percent InSb), and 80.78 percent indium (72.20 percent excess indium). This solution was equilibrated with an immersed InAs substrate oriented in the [111] direction, at 500° C., and was then cooled 20° C. at the natural cooling rate of the furnace of 197° C. per hour.

A single crystal epitaxial layer was grown 42 microns thick and comprising 10 percent InSb and 90 percent InAs as illustrated at point 56 in FIG. 2.

EXAMPLE II

Indium, InSb and sufficient InAs to saturate about 20 grams of indium at 500° C. were melted together to obtain a solution comprising, in mole percentages 78.08 percent indium, 21.18 percent antimony, and 0.74 percent arsenic, as illustrated at point 58 in FIG. 2. The solution was equilibrated with an immersed InAs substrate, oriented in the [111] direction at 500° C., and was cooled 18° C. at a rate of 5° C. per hour.

A single crystal epitaxial layer was grown comprising 24.0 percent InSb and 76.0 percent InAs, as illustrated at point 60 in FIG. 2.

EXAMPLE III

Indium, InSb and sufficient InAs were melted together to obtain a solution comprising, in mole percentages, 75.04 percent indium, 24.30 percent antimony, and 0.66 percent arsenic. The solution was equilibrated with an immersed InAs substrate at 500° C. and was cooled 19° C. at a rate of 1.6° C. per hour.

A single crystal epitaxial layer was grown comprising 50 percent InSb and 50 percent InAs.

EXAMPLES IV-VI

Further similar examples are illustrated in FIG. 2. In all the examples I-VI, and InAs substrate was equilibrated with a solution saturated in InAs at 500° C.

EXAMPLE VII

Indium, InSb, and sufficient InAs to saturate about 20 grams of indium at 400° C. were melted together to obtain a solution comprising, in mole percentages, 91.32 percent indium, 8.6 percent antimony, and 0.08 percent arsenic, as illustrated at point 62 in FIG. 3. The solution was equilibrated with an immersed InAs substrate oriented in the [111] direction at 400° C., and was cooled 40° C. at a rate of 5° C. per hour.

A single crystal epitaxial layer was grown 70 microns thick and comprising 17.5 percent InSb and 82.5 percent InAs as illustrated at point 64 in FIG. 3.

EXAMPLES VIII and IX

Further similar examples are illustrated in FIG. 3. In all the examples VII-IX, InAs substrate was equilibrated with a solution saturated in InAs at 400° C.

EXAMPLE X

A solution of 20 grams of indium and 3 grams of InSb was heated to 300° C., the 3 grams of InSb saturating the solution in InSb at 300° C. An ingot of InAs was positioned in the solution overnight to attempt to saturate the solution in InAs. An InSb substrate was positioned in the solution and the solution temperature was lowered 23° C. at a rate of 6° C. per hour. An epitaxial was formed on the substrate.

We prefer, for making infrared detectors, to obtain an alloy of approximately 50 percent or 60 percent InSb because the alloy exhibits an energy gap minimum of 0.1 ev. at approximately this composition.

It is to be understood that while the detailed drawings and specific examples given describe preferred embodiments of our invention, they are for the purposes of illustration only, that the apparatus of the invention is not limited to the precise details and conditions disclosed, and that various changes may be made therein without departing from the spirit of the invention which is defined by the following claims.

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We claim:

1. A composition of matter comprising a substrate composed of a compound selected from the group consisting of indium arsenide and indium antimonide, having grown thereon a single crystal consisting essentially of a pseudobinary indium arsenide-indium antimonide alloy. 5

2. A composition of matter according to claim 1, wherein the substrate consists essentially of indium arsenide.

3. A composition of matter according to claim 1, 10

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wherein the substrate consists essentially of indium antimonide.

4. An article of manufacture comprising a substrate consisting of a wafer composed of a compound selected from the group consisting of indium arsenide and indium antimonide having grown thereon a single crystal of a pseudobinary indium arsenide-indium antimonide alloy.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,630,693 Dated December 28, 1971

Inventor(s) Jerry W. Moody and Francis J. Reid

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Line 6 of Abstract, "III" should read "[III]".

Column 1, lines 27-28, "arsenic" should read "arsenide".

1, line 69, "a method and a composition for the
epitaxial growth of a solid" should read
"an epitaxially grown solid".

Column 3, line , "1,10 percent" should read "1.10 percent".

Column 4, line 36, "and" should read "an".

4, line 64, "epitaxial was" should read "epitaxial
layer was".

4, line 67, "ev." should read "ev".

Signed and sealed this 27th day of February 1973.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents