

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

DRAWINGS ATTACHED

Method and Apparatus for Growing Semiconductor Crystals

We, TEXAS INSTRUMENTS INCORPORATED, of 6000 Lemmon Avenue, Dallas, Texas, United States of America, a corporation organized and existing under the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method and apparatus for growing compound semiconductor crystals which comprise at least two elements, one more volatile than all the others. The binary compound semiconductors may consist of one of the following element group pairs: Group II and Group VI, Group IV and Group VI, or Group III and Group V (the groups referring to groupings of the periodic tables according to Mendeleeff, as commonly displayed). The ternary compound semiconductors may consist of one of the following element groups, Groups I-III-VI, Groups I-V-VI, and Groups II-IV-VI. Exemplary of two- and three-element compounds semiconductors are InSb, InP, GaAs, AlP, PbTe, InSe, In₂Te₃, AgSbTe₂, Bi₂Te₃, CuFeTe₂, CuGaSe₂, and CuFeSe₃.

The Group III-V compound semiconductor materials are well known. One of the most interesting and useful Group III-V compound semiconductor materials is gallium arsenide and the present invention is particularly useful in growing gallium arsenide crystals from a melt.

The discovery of these "III-V" semiconductor materials for the manufacture of crystals to be used in various electronic devices, such as transistors, has opened many new possibilities in the electronic field, but at the same time has created many new problems. Conventional crystal-pulling pro-

cesses have heretofore utilized an enclosed chamber wherein the crystal melt was maintained, either in a vacuum or in an inert atmosphere, such as argon. It has been found that these conventional processes are not satisfactory when growing a crystal from the "III-V" melts when one of the elements, particularly the Group V element, has a comparatively high volatility. Such is the case when growing a crystal from a melt comprising gallium and arsenic; arsenic has a high volatility at the operating temperatures. In practice, it has been found that the vapour pressure of arsenic over the melt at the melting point of the compound is about 0.9 atmospheres. It is obvious that prior techniques of sending an inert gas into the chamber above the melt would not be satisfactory since the sublimed arsenic would be lost to the atmosphere. Consequently, growing a gallium arsenide crystal has been accomplished in a completely sealed chamber using magnetic coupling of the pull rod to the power drive to avoid risking breaking the seal of the chamber. Whereas this approach is successful from the standpoint of growing a crystal, nevertheless, it is exceedingly difficult to control or operate because of the magnetic coupling. Any attempt to establish a direct drive for the pull rod has met with utter failure, since either air leaked into the system via the drive and destroyed the process, or gas, leaked out of the system via the drive. The corrosive nature of arsenic also is a serious problem as it fouls the drive and its seal at the point of entry into the system. As a result, it was believed that the only successful solution, regardless of the manipulative problems involved and the difficulty of control, was magnetic coupling.

Despite the recognized and admitted difficulties and problems involved in raising

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the crystal from the melt, intensive study and research has finally borne fruit; a method and apparatus according to the present invention have been evolved whereby a direct drive between pull rod and power drive can be used, obviating or mitigating the disadvantages of magnetic coupling.

The present invention is a method of making a semiconductor compound wherein the semiconductor compound is directly pulled from a melt containing the necessary elements and wherein one of the elements possesses a volatility in excess of the other or others, comprising the steps of placing said elements in a chamber and heating to form a melt volatilize said one of said elements and establish an atmosphere in said chamber, which atmosphere includes said one of said elements, maintaining all parts of the chamber which contact the atmosphere above the melt at a temperature sufficiently high to prevent solidifying of the vapour on said parts, permitting an amount of said atmosphere including said one of said elements to leak from the chamber and relieve the pressure therein during said heating step, pulling said semiconductor compound from said melt while permitting an amount of said atmosphere including said one of said elements to leak from the chamber, and trapping the gas permitted to leak from the chamber.

The present invention is also a direct crystal pulling apparatus for making a semiconductor compound comprising a chamber, a crucible supported within said chamber for containing a melt including the necessary elements for making said semiconductor compound, one of said elements possessing a volatility in excess of the other or others, heating apparatus arranged with said chamber for heating said elements to form a melt and volatilize said one of said elements and establish an atmosphere in said chamber, which atmosphere includes said one of said elements and for maintaining all of the parts of the chamber which contact the atmosphere above the crucible at a temperature sufficiently high to prevent solidifying of the vapour on said parts, a crystal puller extending into said chamber for pulling said semiconductor compound from the melt, said chamber being arranged and constructed to permit an amount of said atmosphere including said one of said elements to leak from the chamber and relieve the pressure therein during the establishment of the atmosphere in the chamber and the pulling of said semiconductor compound from the melt, and one or more gas traps arranged exteriorly of the chamber for trapping the gas permitted to leak therefrom.

The present invention is also a direct crystal pulling apparatus making a semiconductor compound comprising a chamber,

a crucible supported within said chamber for containing the necessary elements for making said semiconductor compound, a heating apparatus arranged with said chamber for heating said elements and said chamber, a crystal puller extending through said chamber for pulling a crystal from the elements in said crucible, said puller at its point of entry into said chamber extending through a porous bushing, and a gas trap arranged exteriorly of said chamber in proximity with said porous bushing.

An embodiment of this invention will now be described, by way of example only, with reference to the accompanying drawings, in which:

FIG. 1 is a longitudinal view, partly in section, of a crystal pulling apparatus of this invention;

FIG. 2 is a section of FIG. 1 on the line 2-2 looking in the direction of the arrows;

FIG. 3 is a fragmentary sectional view showing a top-cap sealing arrangement for the crystal puller of FIG. 1;

FIG. 4 is a fragmentary sectional view similar to that shown in FIG. 3 showing an alternative sealing arrangement;

FIG. 5 is a fragmentary sectional view similar to that shown in FIGS. 3 and 4 showing a further sealing arrangement; and

FIG. 6 illustrates schematically a closed system pulling arrangement.

Referring now to Fig. 1, the apparatus illustrated comprises a base 1 upon which is mounted a quartz tube or chamber 2 terminating at its top in a tapered open upper portion 2a. The top of quartz tube 2 can be a flat ground seal rather than tapered. A sealing cap or member 3, preferably of boron nitride, covers the quartz tube. A quartz drive or pull rod 4 connected to rotating and lifting apparatus, designated generally by the reference numeral 30, extends through a boron nitride sealing cap 3 down into the quartz tube 2 and terminates in chuck 5 to which is attached a crystal seed 6. Graphite crucible 8, having a quartz liner 9, contains the charge 7 which is to be melted. As in the usual pulling processes, a seed of semiconductor material of like composition to the melt is lowered into the melt and slowly withdrawn and rotated. When the temperature and pull rate are properly chosen, the melt will crystallize on to the seed to form a single large crystal. The crucible 8 is shown supported within the quartz tube by support 10.

Looking now at the upper part of the drawing, it will be seen that the rod 4 passes through graphite bearing 11 centred in the boron nitride sealing cap 3. A boron nitride sleeve 12 extends upwardly from the cap 3. A quartz tube 13 fits within sleeve 12 and lies spaced from rod 4. The space defined between tube 13 and rod 4 serves

as a trap for trapping the gas permitted to leak from the chamber. Around the area at the upper portion of the drive rod 4 is a water-cooled jacket 17 provided with inlet 18 and outlet 19 for cold water. Above this, a second seal 16, preferably of teflon (Registered Trade Mark), is provided. Insulation cover 15 having an inlet port 14 serves to maintain an inert gas atmosphere around sealing cap 3 and tapered portion 2a. Resistance heater 20 is located within seal 3, resistance heater 21 surrounds the middle of the chamber and R.F. coil 22 surrounds the melt. Thermocouple 23 is provided to maintain the melt at proper temperature.

The operation of the illustrated apparatus for growing gallium arsenide is as follows:

Originally, the chamber is cold and is flushed with an inert gas, for example argon, to provide an inert ambient atmosphere. A quantity of gallium arsenide is placed in the crucible. A quantity of solid arsenic somewhat in excess of that required to give a pressure of one atmosphere when heated to 607°C. is placed in the bottom of the chamber. The chamber 2 is then heated, whereupon the arsenic sublimates and flushes out the argon along with excess arsenic through the planned leakage space between the boron nitride sealing cap 3 and the tapered portion 2a, the joint of which is purposely made less than gastight. An inert gas is maintained in cover 15 to prevent air from diffusing into the chamber. Any arsenic leakage through the bearing 11 condenses above the bearing in the cooler regions, particularly in the quartz arsenic trap 13. When all the arsenic has sublimed, an excess pressure has been relieved through the leaky taper, any further loss of arsenic will be by diffusion through the leaks. This is a relatively slow process, and in practice a satisfactory atmosphere may be maintained in the chamber for several hours. During the procedure just described and during the crystal pulling operation, the entire surface which is in contact with the arsenic atmosphere must be maintained at elevated temperatures (from about 607°C. to about 800°C.) to prevent collection of solid arsenic on the chamber walls. It is to be noted that special resistance heaters 20 and 21, judiciously arranged, have been provided for this explicit purpose.

Although the foregoing discussion and description has been specific to the problems occurring in pulling crystals of Group III-V compound semiconductor materials and in particular in obtaining gallium arsenide crystals, it should be appreciated that the techniques of this invention are in no way limited to these compound semiconductor materials.

The present invention is useful in pulling crystals of any compound semiconductor

material if the compound contains an element more volatile than the others which element has a vapour pressure of one atmosphere or less at the melting point of the compound melt from which a crystal is being pulled.

Group III-V compounds such as InAs and AlAs, as well as InP and GaP, when the more volatile elements exhibit vapour pressures of one atmosphere or less, the compounds may be prepared by the technique of this invention. In some cases, it may be necessary that the compound be a metal-rich melt, which is often the case with phosphorus compounds, before it will exhibit vapour pressure of one atmosphere or less.

Many other binary and ternary compound semiconductor crystals may be prepared by the technique of this invention. Such compound semiconductor materials may be those containing an element from each group in any one of the series of element groupings II-IV, IV-VI, I-III-VI, II-IV-VI, and I-V-VI. Moreover, it should be appreciated that any of the above enumerated compound semiconductor materials may contain various elements in trace impurity or "doping" quantities, as is well known in the art.

Fig. 3, 4 and 5 illustrate gastight sealing arrangements for the top of a closed system crystal puller, useful in place of top sealing cap 3 and tapered section 2a. In this type crystal puller, it is extremely important that the seal be gastight. If air gets into the system, it will destroy the process. For convenience, a top sealing cap 50 and top of the quartz tube 2 are illustrated only, the pull rod, bearings, traps, heaters, etc., being omitted for sake of simplicity.

In Fig. 3, the top edge of tube 2 is flanged at 2b and the top surface 2c is ground optically flat. When a cap 50 of quartz or boron nitride is pressed against the top of tube 2 at surface 2c, a seal will result.

In Fig. 4, the top 2b of tube 2 is likewise flanged and a washer 52, of soft malleable material having a melting point above 607°C., when arsenide is the more volatile element, is positioned on the rim of tube 2. Cap 50 is pressed into contact with the washer to produce a seal. Fig. 5 is similar to Fig. 4, and shows the top of tube 2 as grooved (V shape). An O-ring 54 of soft malleable material, melting above 607°C., is located in the groove, and cap 50 presses against the top of tube 2 to form a seal. Washer 52 and ring 54 may be composed of gold, silver, or platinum or alloys thereof.

The sealing arrangements of Figs. 3 to 5 can be used in the puller described in conjunction with Fig. 1, the puller to be described in conjunction with Fig. 6, or other

system.

Fig. 6 illustrates schematically a puller arrangement including a closed system crystal puller identified generally by the reference numeral 60, a quartz (non contaminating) pull rod 62 extending into the system, a pull mechanism or drive 64 directly coupled to the pull rod 62 and a trap-seal consisting of a graphite bushing 66, a gas-tight seal 68, such as teflon, and structural means 70 to define with the rod 62 and bushing 66 and seal 68 a trap or chamber 72.

If the system of Fig. 6 is used employing a gastight graphite bushing 66 and an arsenic vapour pressure control chamber is interconnected to the closed system, then the trap 72 can be eliminated. The graphite bushing 66 may be made gastight by applying a seal coating 67 (illustrated in dotted lines) where it is exposed to the atmosphere in the closed system 60. For example, a nonporous carbon coating can be used for this purpose. Graphite is the preferred material for bushing 66 or 11, since it is self-lubricating, is operable at temperatures above 600°C., and is soft enough to abrade away and protect the quartz pull rod from solid arsenic. This last feature is important, since arsenic will deposit on the bushing, and would cause severe damage to the pull rod were the bushing not possessed of this property.

WHAT WE CLAIM IS:—

1. A method of making semiconductor compound wherein the semiconductor compound is directly pulled from a melt containing the necessary elements and wherein one of the elements possesses a volatility in excess of the other or others, comprising the steps of placing said elements in a chamber and heating to form a melt and volatilize said one of said elements and establish an atmosphere in said chamber, which atmosphere includes said one of said elements, maintaining all parts of the chamber which contact the atmosphere above the melt at a temperature sufficiently high to prevent solidifying of the vapour on said parts, permitting an amount of said atmosphere including said one of said elements to leak from the chamber and relieve the pressure therein during said heating step, pulling said semiconductor compound from said melt, while permitting an amount of said atmosphere including said one of said elements to leak from the chamber, and trapping the gas permitted to leak from the chamber.

2. A method according to claim 1, wherein said semiconductor compound is gallium arsenide.

3. A direct crystal pulling apparatus for making semiconductor compound comprising a chamber, a crucible supported within

said chamber for containing the necessary elements for making said semiconductor compound, one of said elements possessing a volatility in excess of the other or others, heating apparatus arranged with said chamber for heating said elements to form a melt and volatilize said one of said elements and establish an atmosphere in said chamber which atmosphere includes said one of said elements and for maintaining all of the parts of the chamber which contact the atmosphere above the crucible at a temperature sufficiently high to prevent solidifying of the vapour on said parts, a crystal puller extending into said chamber for pulling said semiconductor compound from the melt, said chamber being arranged and constructed to permit an amount of said atmosphere including said one of said elements to leak from the chamber and relieve the pressure therein during the establishment of the atmosphere in the chamber and the pulling of said semiconductor compound from the melt, and one or more gas traps arranged exteriorly of the chamber for trapping the gas permitted to leak therefrom.

4. A direct crystal pulling apparatus making a semiconductor compound comprising a chamber, a crucible supported within said chamber for containing the necessary elements for making said semiconductor compound, heating apparatus arranged with said chamber for heating said elements and said chamber, a crystal puller extending through said chamber for pulling a crystal from the elements in said crucible, said puller at its point of entry into said chamber extending through a porous bushing, and a gas trap arranged exteriorly of said chamber in proximity with said porous bushing.

5. An apparatus according to claim 3 or 4, wherein said chamber comprises an open upper portion engaged by a member through which said crystal puller extends.

6. An apparatus according to claim 4 or claim 5, wherein said porous bushing is made of graphite.

7. An apparatus according to claim 6, wherein said crystal puller is made of quartz.

8. A semiconductor compound when produced by the method of claim 1 or 2.

9. A method of producing a semiconductor compound as substantially described herein with reference to the accompanying drawings.

10. A direct crystal pulling apparatus for producing a semiconductor compound substantially as described herein with reference to the accompanying drawings.

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system.

Fig. 6 illustrates schematically a puller arrangement including a closed system crystal puller identified generally by the reference numeral 60, a quartz (non contaminating) pull rod 62 extending into the system, a pull mechanism or drive 64 directly coupled to the pull rod 62 and a trap-seal consisting of a graphite bushing 66, a gas-tight seal 68, such as teflon, and structural means 70 to define with the rod 62 and bushing 66 and seal 68 a trap or chamber 72.

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2. A method according to claim 1, wherein said semiconductor compound is gallium arsenide.

3. A direct crystal pulling apparatus for making semiconductor compound comprising a chamber, a crucible supported within

said chamber for containing the necessary elements for making said semiconductor compound, one of said elements possessing a volatility in excess of the other or others, heating apparatus arranged with said chamber for heating said elements to form a melt and volatilize said one of said elements and establish an atmosphere in said chamber which atmosphere includes said one of said elements and for maintaining all of the parts of the chamber which contact the atmosphere above the crucible at a temperature sufficiently high to prevent solidifying of the vapour on said parts, a crystal puller extending into said chamber for pulling said semiconductor compound from the melt, said chamber being arranged and constructed to permit an amount of said atmosphere including said one of said elements to leak from the chamber and relieve the pressure therein during the establishment of the atmosphere in the chamber and the pulling of said semiconductor compound from the melt, and one or more gas traps arranged exteriorly of the chamber for trapping the gas permitted to leak therefrom.

4. A direct crystal pulling apparatus making a semiconductor compound comprising a chamber, a crucible supported within said chamber for containing the necessary elements for making said semiconductor compound, heating apparatus arranged with said chamber for heating said elements and said chamber, a crystal puller extending through said chamber for pulling a crystal from the elements in said crucible, said puller at its point of entry into said chamber extending through a porous bushing, and a gas trap arranged exteriorly of said chamber in proximity with said porous bushing.

5. An apparatus according to claim 3 or 4, wherein said chamber comprises an open upper portion engaged by a member through which said crystal puller extends.

6. An apparatus according to claim 4 or claim 5, wherein said porous bushing is made of graphite.

7. An apparatus according to claim 6, wherein said crystal puller is made of quartz.

8. A semiconductor compound when produced by the method of claim 1 or 2.

9. A method of producing a semiconductor compound as substantially described herein with reference to the accompanying drawings.

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