

PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Method of Producing Specified III—V Compounds

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 of producing a compound of an element from the sub-grouping of Group III elements that includes gallium and aluminium (hereinafter and in the claims called "specified Group III sub-grouping"), and an element from the sub-grouping of Group V elements that includes arsenic and phosphorus (hereinafter called "specified group V sub-grouping").

A compound of an element from the specified Group III sub-grouping and an element from the specified Group V sub-grouping will hereinafter and in the claims be referred to as "specified III—V compound". Gallium arsenide is exemplary of a specified III—V compound.

Specified III—V compounds are customarily produced by a variety of methods. For instance, gallium arsenide is customarily produced by reacting liquid gallium with arsenic in the vapour stage at a temperature at least as high as the melting point of gallium arsenide. However, this method has the disadvantage of requiring a high temperature which increases the susceptibility toward contamination. In addition, this method is not readily adaptable as a continuous production process.

In an effort to overcome the above-mentioned disadvantages, it has been suggested that gallium arsenide be prepared by reducing gallium oxide with a gaseous stream of heated hydrogen and arsenic vapours. Another suggested technique has been to volatilize gallium and arsenic and thereafter codeposit on

a relatively cooled surface to form the gallium arsenide.

Each of the above-mentioned techniques, as well as other techniques known to the art, are subject to their own difficulties. The hydrogen reduction of gallium oxide is difficult to complete, and the resulting compound semiconductor is heavily contaminated with oxygen. Similarly codeposition of gallium and arsenic is unusually difficult to control because of the difference in volatility of the two ingredients.

An object of the present invention is to provide an improved process for production of specified III—V compounds.

The present invention is a method of producing a specified III—V compound which comprises passing a vapour phase mixture of hydrogen and the chlorides of one of the elements of the specified group III sub-grouping and one of the elements of the specified group V sub-grouping into a high temperature zone, the temperature being sufficiently high so that the hydrogen reacts with the chlorides; thereafter passing the still vapour phase mixture into contact with a condensing surface maintained at a lower temperature which is sufficiently low so that the Group III and Group V elements deposit in solid form as a relatively non-volatile compound; and removing the gaseous unreacted hydrogen, unreacted chlorides and hydrogen chloride.

The present invention is also a method of producing gallium arsenide which comprises passing a vapour phase mixture of hydrogen, gallium trichloride, and arsenic trichloride through a reaction zone maintained at a temperature exceeding 900°C, whereby the hydrogen reacts with the chlorides; thereafter passing the gaseous mixture into contact with a surface maintained at a temperature of from 200°C to 900°C, whereby gallium arsenide condenses in solid phase onto said surface;

and removing the gaseous unreacted hydrogen, unreacted chlorides and hydrogen chloride.

Embodiments of the present invention will now be described, by way of example, with reference to the accompanying drawing, in which:

Figs. 1 to 3 schematically illustrate apparatus used in carrying out methods according to the invention.

Briefly stated, the present invention involves the process of simultaneous reduction of an element of the specified group III sub-grouping, or a chloride of said element, and of an element of the specified group V sub-grouping, or a chloride of said element, to produce a compound of the two elements. In a preferred embodiment, the invention involves producing the compound by the vapour phase reduction of arsenic halide by hydrogen in the presence of gallium halide or metallic gallium under conditions whereby the gallium arsenide is stoichiometrically produced.

According to one method of production according to the present invention, a mixture of arsenic trichloride and gallium trichloride is introduced into a stream of hydrogen in excess of that required for complete reduction of the chlorides. The gaseous mixture is then passed through a hot reaction zone.

It is theorized that in the hot reaction zone the hydrogen reduces the arsenic trichloride to free arsenic. The combination of high temperatures and low partial pressure keep the arsenic in the vapour phase. It is thought that the gallium trichloride reacts with the hydrogen to form gallium dichloride. Free gallium is not formed in the hot reaction zone, and any free gallium produced immediately reacts with the various chlorides present to form a chloride of gallium which is reduced to the more stable gallium dichloride. There is no gallium arsenide deposited because under these conditions, any gallium arsenide produced would be unstable.

Thereafter, the gases are passed into contact with a cool surface maintained at a temperature of from 200 to 900°C. The gallium dichloride disproportionates and the gallium combines with the free arsenic to form gallium arsenide which deposits in solid form. It is important to note that the deposition temperature is still high enough to maintain the other components of the gas stream in vapour phase, namely, hydrogen and hydrogen chloride which are gaseous even at room temperature, and unreacted gallium and arsenic chlorides as well. Thus, pure gallium arsenide is deposited. Desirably, the temperature of the gallium arsenide crystals is maintained high enough to also keep any excess arsenic from depositing on the crystal product.

An extremely close control of product purity is possible when the compound semiconductor is produced in accordance with the

process of the present invention. Due allowance for the relative volatility of the gallium and the arsenic in vapour phase at the cool condensation point can be made by employing arsenic in excess so that an amount of arsenic can remain in the vapours at the condensation temperature and not thereby upset the stoichiometric ratio of gallium and arsenic required for gallium arsenide. Similarly, a measure of control is afforded by variation in the reaction temperature and the condensation temperature or by operating at a higher or lower hydrogen gas pressure and even at a different ratio of hydrogen to reactants. A preferred ratio is 1.75:1.0.

Although the above-described process embodies important advantages, it has been found that the utilization of gallium trichloride as an initial constituent presents problems in that gallium trichloride readily hydrolyzes with moisture and is very corrosive. In a second embodiment of the invention, such problems are minimized by forming the gallium trichloride in the reaction chamber. According to this second mode, the gaseous stream which contains only the hydrogen and arsenic trichloride is passed into contact with liquid gallium heated to above 900°C. At this reaction temperature, the arsenic trichloride is reduced by the hydrogen to elemental arsenic vapours and HCl. The HCl produced when the $AsCl_3$ is reduced reacts with the liquid gallium to produce gallium trichloride. This reaction continues until all of the gallium is converted to gallium trichloride. Gallium arsenide is then produced by the same mechanism described in the first embodiment of the invention.

Although the foregoing description has been largely given in terms of the production of gallium arsenide, it should be noted that other specified III—V compounds can be similarly produced by employment of other combinations of reactants, being elements or chlorides of elements one from each of the specified Groups III and V sub-groupings, for example chlorides of aluminium and phosphorus could be employed to produce aluminium phosphide and other combinations of the reactants named could be employed to produce aluminium arsenide and gallium phosphide.

For a further understanding of the invention, the following specific examples are presented.

EXAMPLE I

Apparatus as shown in Fig. 1 is used. The apparatus consists of a quartz tube 10 (25 mm O.D.; 22 mm I.D.) having an inlet 11 connected to a suitable hydrogen supply and an exhaust outlet 12. Heaters 14 and 15 are provided to maintain the temperatures noted in the legend. A flask 18 terminating in a dripper 20 is positioned in a branch tube 22 adjacent one end of tube 10. In conducting the process of the invention, hydrogen

is admitted through inlet 11 at about 100 cc/min. (0.0045 moles/min.). The flask 18 contains a mixture of GaCl_3 and AsCl_3 in the weight ratio of 37.5 to 50. The dripper 20 is controlled to give a drip rate of about 0.2 cc/min. corresponding to about 0.44 g/min. (average specific gravity 2.2) and about 0.00244 moles/min., assuming an average molecular weight of 180. This gives a mole ratio in the reaction zone of $\frac{\text{H}_2}{x} = 1.84$ where x equals GaCl_3 and AsCl_3 . Gallium arsenide is deposited in the region of tube 10 within heater 15.

EXAMPLE II

Apparatus as shown in Fig. 2 is used. The tube 30 is the same as tube 10. A flask 32 attached to tube 30 contains AsCl_3 at 100°C . A flask 34 similarly attached contains GaCl_3 at 100°C . Hydrogen is blown through the two flasks at about 400 cc/min. to cause a vapor pressure of 20 mm for GaCl_3 and 400 mm for AsCl_3 . The mole ratio of AsCl_3 to GaCl_3 is 20 to 1 and of $\frac{\text{H}_2}{x}$ (where x is AsCl_3 plus GaCl_3) is 2.5. Gallium arsenide is deposited in the rightmost region of tube 30.

EXAMPLE III

Apparatus as shown in Fig. 3 is used. A tube 40 like tubes 10 and 30 is employed. A flask 42 is attached at one end of tube 40 and contains AsCl_3 . A boat 44 of liquid gallium is located in tube 40. Hydrogen is bubbled through the AsCl_3 and also admitted to the end of tube 40. Hydrogen flow is about 1 litre/min. The mole ratio of H_2 to AsCl_3 is about 76 to 1. Gallium arsenide is deposited at the right end of tube 40.

WHAT WE CLAIM IS:—

1. A method of producing a specified III—V compound which comprises passing a vapour phase mixture of hydrogen and the chlorides of one of the elements of the specified group III sub-grouping and one of the elements of the specified Group V sub-grouping into a high temperature zone, the temperature being sufficiently high so that the hydrogen reacts with the chlorides; thereafter passing the still vapour phase mixture into contact with a condensing surface maintained at a lower tem-

perature which is sufficiently low so that the Group III and Group V elements deposit in solid form as a relatively non-volatile compound; and removing the gaseous unreacted hydrogen, unreacted chlorides and hydrogen chloride.

2. The process of producing gallium arsenide which comprises passing a vapour phase mixture of hydrogen, gallium trichloride, and arsenic trichloride through a reaction zone maintained at a temperature exceeding 900°C , whereby the hydrogen reacts with the chlorides, thereafter passing the gaseous mixture into contact with a surface maintained at a temperature of from 200°C to 900°C , whereby gallium arsenide condenses in solid phase onto said surface; and removing therefrom the still gaseous hydrogen, hydrogen chloride and unreacted chlorides.

3. The process of claim 2 wherein arsenic trichloride is present in excess of stoichiometric requirement for gallium arsenide.

4. The process of claim 2 wherein the hydrogen is present in the ratio by volumes of better than 1.75:1 to the mixture of arsenic trichloride and gallium trichloride.

5. A method for the production of gallium arsenide which comprises forming a vapour phase mixture of arsenic trichloride in hydrogen, passing said mixture into contact with liquid gallium maintained at a temperature in excess of 900°C whereby a chloride of gallium is formed, reacting said arsenic trichloride and chloride of gallium with hydrogen, and thereafter passing the still vapour phase mixture into contact with a surface maintained at a temperature of from 200°C to 900°C whereby gallium arsenide condenses in solid phase onto said surface, and removing therefrom the still gaseous hydrogen, hydrogen chloride, and unreacted chlorides.

6. A method of producing gallium arsenide substantially as hereinbefore described in Example I, II or III.

7. Gallium arsenide when produced by any of the methods of claim 6 or its obvious chemical equivalent.

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Reference has been directed in pursuance of Section 9, subsection (1) of the Patents Act, 1949, to patent No. 944,872.



- is admitted through inlet 11 at about 100 cc/min. (0.0045 moles/min.). The flask 18 contains a mixture of GaCl_3 and AsCl_3 in the weight ratio of 37.5 to 50. The dripper 20 is controlled to give a drip rate of about 0.2 cc/min. corresponding to about 0.44 g/min. (average specific gravity 2.2) and about 0.00244 moles/min., assuming an average molecular weight of 180. This gives a mole ratio in the reaction zone of $\frac{\text{H}_2}{x} = 1.84$ where x equals GaCl_3 and AsCl_3 . Gallium arsenide is deposited in the region of tube 10 within heater 15.

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perature which is sufficiently low so that the Group III and Group V elements deposit in solid form as a relatively non-volatile compound; and removing the gaseous unreacted hydrogen, unreacted chlorides and hydrogen chloride.

2. The process of producing gallium arsenide which comprises passing a vapour phase mixture of hydrogen, gallium trichloride, and arsenic trichloride through a reaction zone maintained at a temperature exceeding 900°C , whereby the hydrogen reacts with the chlorides, thereafter passing the gaseous mixture into contact with a surface maintained at a temperature of from 200°C to 900°C , whereby gallium arsenide condenses in solid phase onto said surface; and removing therefrom the still gaseous hydrogen, hydrogen chloride and unreacted chlorides.

3. The process of claim 2 wherein arsenic trichloride is present in excess of stoichiometric requirement for gallium arsenide.

4. The process of claim 2 wherein the hydrogen is present in the ratio by volumes of better than 1.75:1 to the mixture of arsenic trichloride and gallium trichloride.

5. A method for the production of gallium arsenide which comprises forming a vapour phase mixture of arsenic trichloride in hydrogen, passing said mixture into contact with liquid gallium maintained at a temperature in excess of 900°C whereby a chloride of gallium is formed, reacting said arsenic trichloride and chloride of gallium with hydrogen, and thereafter passing the still vapour phase mixture into contact with a surface maintained at a temperature of from 200°C to 900°C whereby gallium arsenide condenses in solid phase onto said surface, and removing therefrom the still gaseous hydrogen, hydrogen chloride, and unreacted chlorides.

6. A method of producing gallium arsenide substantially as hereinbefore described in Example I, II or III.

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