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APPARATUS FOR THE PREPARATION OF SEMICONDUCTOR MATERIAL

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2 Claims. (Cl. 23-277)

This invention relates to growth of semiconductor material from the vapor phase and more particularly, to an apparatus for making bulk semiconductor material in a continuous manner.

It is known in the art to prepare semiconductor materials by vapor deposition upon a starting element, or substrate, which is heated to a temperature at which deposition can occur thereon. For example, Group III-V semiconductor compounds are prepared by a batch process from the vapor phase involving a disproportionation reaction which transfers material from a hot to a cold zone, the thermal gradient being provided by a furnace.

Accordingly, it is an object of the present invention to provide an apparatus for growing bulk semiconductor material from the vapor phase.

Another object of this invention is to provide bulk semiconductor material by a continuous, open tube process.

A further object of the instant invention is to provide Group III-V semiconductor rods in a continuous manner by growth from the vapor phase.

A feature of the present invention is the provision of a retractable cold pedestal having a semiconductor seed member thereon for growing elongated, bulk semiconductor material from the vapor phase in a continuous manner.

Another feature of this invention is the provision of a continuous feed system for supplying metallic reactant material in the preparation of Group III-V semiconductor material by growth from the vapor phase.

Still another feature is the provision of a withdrawal mechanism for growing bulk semiconductor material in a continuous manner.

These and other objects will be made apparent from the following more detailed description of the invention, in which reference will be made to the accompanying drawing, in which:

The figure is a schematic illustration of the apparatus of the present invention.

In accordance with the present invention, there is provided an apparatus for making bulk semiconductor Group III-V compounds of the general formula:



where A and B are different elements but both of Group III, i.e., boron, aluminum, gallium or indium, and C and D are different elements but both of Group V, i.e., nitrogen, phosphorus, arsenic or antimony; where subscripts x and y denote atom proportions whose values can change from zero to unity, inclusive, in a continuous and controlled manner.

Referring now to the figure, there is shown schematically the apparatus for forming bulk semiconductor material according to the present invention. The apparatus includes reaction chamber 1 which is formed of a suitable material, such as quartz, and is in the form of an open tube having an inlet 2 and an outlet 3. Surrounding the tube is a furnace 4 which may be used to preset the temperature within the reaction chamber in a given manner. For example, the furnace may be maintained at an elevated temperature so that the reactants are in the vapor state. The furnace may conveniently comprise an elec-

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trical insulating ceramic shell such as Alundum in which are embedded resistance heating wires, spirally wound, all forming a cylindrical heating device within which the reaction chamber may be positioned. The resistance heating wire of the furnace may be connected to a source of electrical energy through each of the furnace's individual terminal wires.

For purposes of clarity only, and not as a limitation thereof, the following description of the present invention will be described with particular reference to the formation of gallium phosphide material.

Into the reaction chamber 1 is introduced an elemental or metallic constituent of the semiconductor, illustrated as 5, contained within a boat 6, suitably one made of vitreous carbon material; the material may be continuously fed into the chamber from reservoir 7.

A supply line, generally indicated as 8, is provided at the inlet part 2 of the open tube vessel for admission of gaseous reactants into the reaction chamber. For example, if it is desired to form bulk gallium phosphide material, the metallic constituent 5 is gallium. A phosphorus halide, illustrated as 9, such as phosphorus trichloride, serves as a transport agent for the non-metallic constituent. The transfer agent is admitted into the reaction chamber in a stream of H₂.

Within the reaction furnace is placed a support element 10. Positioned on the support is a single crystal semiconductor starting or seed member 11. As shown in the figure, the support is in the form of a pedestal. Within the pedestal element is a duct 12 for admitting a cooling gas 13, such as nitrogen, therethrough. As the cooling gas leaves exit nozzle 14 of duct 12, it circulates around and cools seed 11 to a low temperature. The gases are continuously circulated around the pedestal element in the direction indicated by arrow 15.

Cooling of the seed in the manner described above provides a cold site within the reaction chamber at which formation of gallium phosphide may occur by disproportionation of the intermediate reactive species thereof.

The layer which forms on the single crystal substrate member by this technique is an epitaxial crystal. When the substrate semiconductor material is the same as the material being deposited from the vapor phase, the epitaxial layer has the same chemical constitution as the substrate but may differ in conductivity type or degree as desired. On the other hand, when the substrate and vapor materials are different chemically, then the first epitaxial layers are generally a solid solution of the substrate and vapor depositing materials, while the rest of the rod is of the latter only.

Generally the pedestal is maintained at a temperature of between 800-900° C. for the preparation of Group III-V semiconductor material. Preferably it is at 850° when gallium phosphide material is produced.

As the deposited material increases in length, a bulk rod is obtained. As the rod is extended, it is necessary to retract the pedestal at a rate approximately equal to the rate of growth of the rod so that an elongated rod can be produced with a smaller reaction vessel. As withdrawal mechanism 16 is provided for the purpose of pulling the pedestal downward in the direction of arrow 17. Generally the pedestal is retracted at a rate of about 10 mils per hour. There is thus provided an elongated bulk rod of single crystal semiconductor material.

Example 1

Using the apparatus of the figure, high purity gallium metal of semiconductor grade is charged in a vitreous carbon boat and inserted in a 1" O.D. quartz tube, which, in turn, is inserted in an 18" globar furnace preset at about 1000° C. The quartz tube then is connected to a gas entrance line and a gas exit line. Hydrogen then is passed

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through the system at 170 ml./min. for two hours in order to remove moisture and oxide films on the molten gallium. A flask which is charged with 5 l. of reagent grade phosphorus trichloride is immersed in ice water at 0° C. The hydrogen gas is passed through the phosphorus trichloride at 70 ml./min. for an extended length of time. The vapor pressure of phosphorus trichloride at 0° C. is 35 mm. The seed member is single crystal gallium phosphide. Gaseous nitrogen gas is continuously circulated at a flow rate of 5 l./min. in the pedestal member to maintain the substrate of about 850° C. At the end of the run there is observed a built-up rod of gallium phosphide on the gallium phosphide seed. The gas input feed is then switched to helium and the tube is cleaned of excess phosphorus trichloride and gallium chloride which are formed during the reaction. The withdrawal mechanism retracts at a rate of 10 mils per hour. At the conclusion of the run, the tube is opened while excluding air, cooled to room temperature, and the elongated gallium phosphide rod is removed.

Example 2

The procedure of Example 1 is followed using indium metal in place of gallium metal and an indium phosphide seed at 800° C. in place of a gallium phosphide seed to produce an elongated rod of indium phosphide.

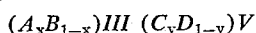
Example 3

The procedure of Example 1 is followed using arsenic trichloride in place of phosphorus trichloride to produce an elongated rod of gallium arsenide.

While the invention has been described with reference to certain preferred embodiments thereof, it will be understood that changes and modifications may be made which are within the skill of the art.

What is claimed is:

1. Apparatus for the formation of bulk semiconductor material of the general formula:



where A and B are different elements but both of Group III and C and D are different elements but both of Group V and where subscripts x and y denote atom proportions whose values are zero to unity, inclusive, which comprises:

(a) an open reaction chamber,

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- (b) a boat within said chamber,
- (c) means for continuous charging of said boat with the metallic element of the specific material to be formed,
- (d) means for heating said metallic element to a predetermined temperature adequate to transform said element to the vapor phase,
- (e) a transport gas for said non-metallic element,
- (f) a pedestal support element within said chamber for supporting a wafer,
- (g) cooling means positioned in said support for cooling said wafer to a temperature in the range 800°-900° C. where deposition can occur thereon, and
- (h) withdrawal means associated with said pedestal for retracting the same at about the same rate as that at which Group III-V material is built-up on said seed.

2. Apparatus for the formation of gallium phosphide, which comprises:

- (a) an open reaction chamber containing a boat adapted to be charged with gallium metal,
- (b) means for continuously charging said boat with gallium metal,
- (c) a furnace for heating said gallium to above 1000° C. to transform said gallium to the vapor phase,
- (d) a phosphorus trichloride transport agent for said non-metallic element,
- (e) a pedestal within said chamber,
- (f) a single crystal gallium phosphide seed member positioned on said support,
- (g) nitrogen cooling gas circulating within said pedestal for cooling said seed to a temperature of about 850° C. where deposition can occur thereon, and
- (h) withdrawal means for retracting said pedestal at a rate of about 10 mils per hour.

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