

Jan. 14, 1969

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3,421,952

METHOD OF MAKING HIGH RESISTIVITY GROUP III-V COMPOUNDS
AND ALLOYS DOPED WITH IRON FROM AN IRON-ARSENIDE SOURCE
Filed Feb. 2, 1966

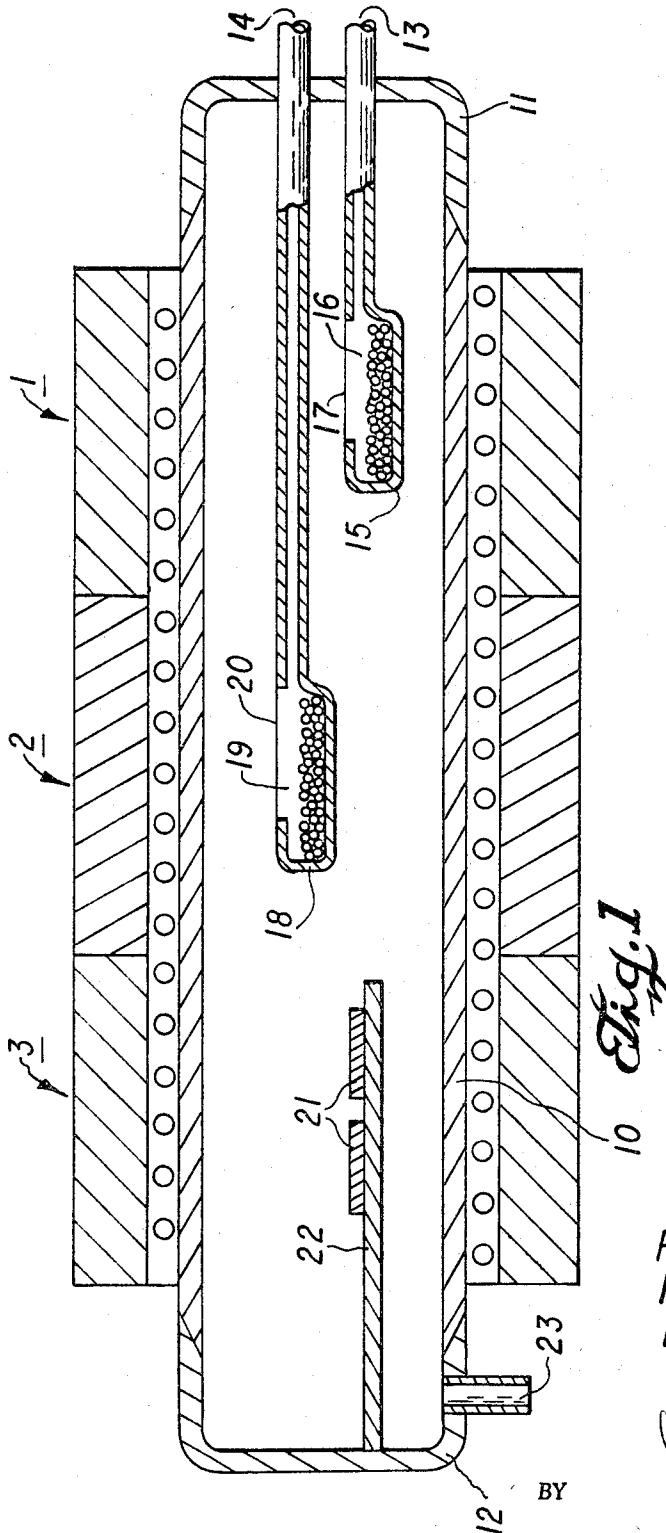


Fig. 1

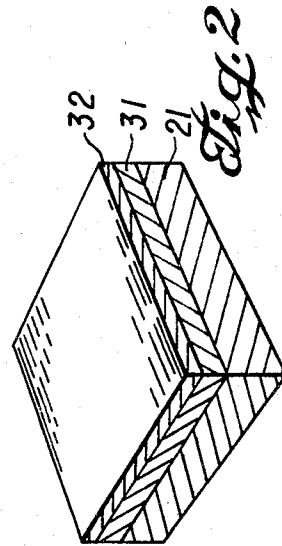


Fig. 2

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METHOD OF MAKING HIGH RESISTIVITY GROUP III-V COMPOUNDS AND ALLOYS DOPED WITH IRON FROM AN IRON-ARSENIDE SOURCE

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Filed Feb. 2, 1966, Ser. No. 524,538

U.S. Cl. 148—175
Int. Cl. H011 7/00

9 Claims

This invention relates to high resistivity or semi-insulating Group III-V compounds and alloys and methods of making same. More particularly, it relates to a method of producing epitaxial deposits of high resistivity Group III-V compound materials through the vapor phase reaction of Group III and Group V elements while simultaneously doping with appropriate impurities to produce epitaxial deposits with resistivities of about 10^3 ohm-cm. or greater.

As used herein, the terms "high resistivity Group III-V materials" and "semi-insulating Group III-V materials" are used to refer to compounds of one or more elements from Group III of the Periodic Table with one or more elements of Group V of the Periodic Table, said compounds having a resistivity of the order of 10^3 ohm-cm. or higher. The terms refer to ternary and quaternary compounds and alloys of the Group III-V compounds as well as binary compounds of Group III and Group V elements.

Semi-insulating Group III-V compound crystals have been produced by withdrawing a crystalline seed from an appropriately doped melt of the semiconductor material. Pulled crystals of semi-insulating gallium arsenide, for example, may be formed by doping a GaAs melt with oxygen, iron or chromium. In the past, however, epitaxial deposits of uniformly high resistivity Group III-V materials could not be controllably produced. Various attempts to dope Group III-V epitaxial deposits with oxygen, iron or chromium during the production thereof to produce controlled deposits of uniformly high resistivity monocrystalline Group III-V materials have been generally unsuccessful. Apparently the presence of oxygen in an epitaxial reactor in amounts sufficient to dope the deposit to high resistivity interferes with the formation of monocrystalline deposits. Chromium and iron, although known for their ability to form semi-insulating III-V crystals grown from a melt, could not be included in sufficient amounts in epitaxial deposits to dope the deposit to high resistivities.

It is therefore an object of this invention to provide a method of making epitaxial monocrystalline layers of high resistivity Group III-V materials. Another object is to provide epitaxial layers of semi-insulating Group III-V materials on semiconductor substrates and to make composite structures of alternate layers of high resistivity and semiconducting materials. Still another object is to provide a method of doping III-V epitaxial deposits with iron in sufficient quantities to produce monocrystalline epitaxial deposits with resistivities of 10^3 ohm-cm. or higher.

In accordance with this invention semi-insulating epitaxial deposits are formed by doping epitaxially formed Group III-V compounds with iron. Iron is incorporated into the epitaxial deposit during the growth of the epitaxial material from a source of iron arsenide. The iron arsenide is formed within the epitaxial reactor prior to the deposition of the Group III-V compound by a "pre-arseniding" step described hereinafter.

A particular advantage of this invention is the production of alternate layers of semi-insulating and low resistivity semiconducting material in the same monocrystalline wafer, thus providing electrical isolation between

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alternate layers of semiconducting material in a monocrystalline block. Other objects, features and advantages of the invention will become more readily understood from the following detailed description taken in conjunction with the appended claims and attached drawing, in which:

FIGURE 1 is an elevational view partially in section of an epitaxial reactor suitable for practicing the invention and

FIGURE 2 is a perspective view in section of a monocrystalline wafer containing alternate layers of semi-insulating and semiconducting Group III-V compound materials.

The epitaxial reactor shown in FIGURE 1 comprises an elongated cylindrical chamber 10 having end caps 11 and 12 fitted thereon. End cap 11 carries feed tubes 13 and 14 passing therethrough into the interior of chamber 10.

A boat-like container 15 is attached to the end of feed tube 13, such that feed gases passing through feed tube 13 into the interior of the chamber 10 pass over or through an iron source 16 contained in the container 15. The container has an opening 17 to allow gases passing over or through the material 16 within the container to exit into the interior of chamber 10. Likewise, a similar boat-like container 18 attached to the end of feed tube 14 contains a Group III feed material 19. The Group III feed material may be either elemental Group III element or a compound thereof or alloys of a plurality of Group III elements. Container 18 is also attached in a manner so as to allow gases entering through feed tube 14 to pass over or through the feed material 19 before exiting into the interior of chamber 10 through opening 20. Substrate wafers 21 are positioned within the chamber 10 on a substrate holder 22 mounted within end cap 12. End cap 12 is also provided with an exhaust outlet 23 through which spent gases exit from the reactor chamber 10.

The reactor chamber 10 is positioned partially within a furnace having three separately controlled temperature zones, generally indicated by the reference characters 1, 2 and 3. The heating elements of each of the zones of the furnace are individually controlled by conventional means (not shown) so that the temperature in each zone may be individually and separately controlled to provide the desired temperature within each zone of the furnace. The boat-like container 15 containing the iron source 16, the feed container 18, and the substrate wafers 21 are appropriately positioned within zones 1, 2 and 3 of the reactor, respectively. Consequently, the temperature of the iron feed material within the reactor chamber 10 is controlled by the temperature of furnace zone 1. Likewise the Group III feed material 19 is maintained at the temperature of furnace zone 2, and the temperature of the substrates 21 is determined by the temperature of furnace zone 3.

The operation of the apparatus of FIGURE 1 to produce epitaxial deposits of semi-insulating Group III-V compounds is discussed hereinafter with specific reference to the production of semi-insulating gallium arsenide. However, it is to be understood that the description given is merely by way of example, and that the principles of operation are equally applicable to other Group III-V compounds and ternary and quaternary alloys thereof.

With the exception of the iron doping step, as hereinafter described, operation of the apparatus of FIGURE 1 is similar to the operation of conventional epitaxial reactors. Epitaxial deposits of gallium arsenide are conventionally formed by vapor phase reaction of gallium and arsenic in a thermal gradient to produce low resistivity gallium arsenide deposits on the surface of the substrate. Zones 2 and 3 of the furnace in the reactor shown in FIGURE 1 and the apparatus contained therein are typical of the conventional epitaxial reactor. An arsenic-

containing gas such as arsine (AsH_3) or arsenic trichloride (AsCl_3) is entrained in a carrier gas, usually hydrogen. The arsenic-containing gas is fed into the reaction tube 10 through inlet 14 and allowed to pass over feed material 19, either gallium or gallium arsenide, contained in the boat-like container 18. The container 18 is maintained at a temperature of about 800–1100° C. Halide vapor produced by the reduction of AsCl_3 or supplied separately reacts with the gallium source 19 and forms a volatile chloride of gallium which is then transported from the container 18 through exit 20 and into the reaction chamber.

The Group V element such as arsenic may be admitted through tube 14 in the form of vapors of arsenic trichloride or any other suitable volatile compound of arsenic. Alternatively, arsenic may be admitted into the reactor through a separate inlet tube (not shown) in the form of a suitable volatile hydride or halide of arsenic or in the form of elemental vaporized arsenic transported in a carrier stream such as hydrogen. The resultant gaseous mixture contains elemental arsenic and a volatile halide of gallium which then flows through a decreasing temperature gradient into zone 3 of the furnace. The volatile gallium halide disproportionates into gallium trihalide and free gallium. The free gallium reacts with the free arsenic to form a monocrystalline epitaxial layer of gallium arsenide on the substrates 21.

In accordance with a specific embodiment of this invention, the epitaxial gallium arsenide deposit formed as described above is doped with iron. High purity iron 16 is placed in container 15 within zone 1 of the furnace of FIGURE 1. Purified gallium 19 is placed in container 18 and suitable substrates 21 such as monocrystalline gallium arsenide wafers are positioned on the substrate holder 22 within the reactor 10. The reactor is closed and flushed with hydrogen to remove oxygen and water vapors from the reactor chamber. Individual controls are activated to raise the temperatures of the furnace zones 1, 2 and 3 to the desired temperatures for the production of gallium arsenide. The temperature of zone 1 is raised to about 900° C. to 950° C. Zone 2 is maintained at about 800° C. to 1100° C. and zone 3 is maintained at about 500° C. to 800° C. An arsenic-containing gas such as arsine, arsenic trichloride or elemental arsenic vapors entrained in a suitable carrier such as hydrogen is admitted through inlet tube 13 and passed over the purified iron 16 in container 15. The arsenic reacts with the iron to form an arsenic-iron compound (FeAs or FeAs_2). This step is referred to as "pre-arseniding" the iron.

It has been found that iron will not be satisfactorily included in the epitaxial deposit unless pre-arsenided. Presumably, elemental iron is not transported in sufficient quantities to dope the epitaxial deposit; but iron reacts with arsenic to form a volatile iron arsenide compound which is transported to the deposition zone by a suitable carrier gas and is included in the deposit, thereby doping the epitaxial deposit with iron. The amount of iron included in the epitaxial deposit, and thus the resistivity of the epitaxial deposit, is controlled by controlling the relative flow rates of carrier gases used for transporting the gallium, arsenic and iron arsenide. The iron arsenide is preferably formed in the reactor immediately prior to use as described above in order to insure purity of the iron source and avoid contamination. However, other sources of iron arsenide may be substituted. Furthermore, the iron arsenide is conveniently transported in a carrier gas containing arsenic, thus replacing iron arsenide removed by the carrier gas.

EXAMPLE I

About 30 grams of elemental gallium was placed in container 18 of the reactor shown in FIGURE 1. About 200 mgs. of purified iron was placed in container 15. The reactor was closed and flushed with hydrogen. With hydrogen in the reactor, furnace zones 1, 2 and 3 were ac-

tivated so as to produce temperatures of 950° C., 950° C. and 750° C. in the iron, feed and substrate zones respectively. A gaseous mixture of about 2% AsCl_3 in hydrogen was admitted through feed tube 13 at a rate of about 50 cc./min. These conditions were maintained for 3 hours, during which time the iron in boat 15 was converted to iron arsenide.

After the iron had been converted, the reactor was cooled, flushed with helium and a monocrystalline wafer of GaAs 21 placed on substrate holder 22. The reactor was closed and flushed with hydrogen. The furnace zones were activated to produce the same temperatures as before. A gaseous mixture of about 2% AsCl_3 in H_2 was passed through feed tube 14 at a rate of about 80 cc./min. The flow of AsCl_3 in H_2 through feed tube 13 was reduced to 12 cc./min. Under these conditions an iron-doped epitaxial layer of GaAs was deposited on substrate 21 at a rate of about 0.3 microns/min. The epitaxial layer was examined and found to be P-type with a resistivity of 10^5 ohm-cm. at room temperature. The epitaxial layer was monocrystalline and uniform in composition and conductivity.

The wafer of FIGURE 2 is illustrative of the composite structures which can be made utilizing the invention. The wafer is comprised of a plurality of monocrystalline layers 31 and 32 epitaxially deposited on a substrate 21. The substrate 21 may be a monocrystalline III-V compound semiconductor wafer or ternary or quaternary alloy. The substrate may also be germanium or silicon or any of the II-VI compounds with crystalline lattice spacings closely approximate to that of the epitaxial material to be formed. Furthermore, the substrate 21 may be N-type, P-type or semi-insulating material. As shown in FIGURE 2, a plurality of layers 31 and 32 may be epitaxially formed on the substrate 21. For example, substrate 21 may be low resistivity N-type GaAs. Epitaxial layer 31 may be formed thereon as described above in Example I to produce an epitaxial layer 31 of semi-insulating GaAs. A second layer 32 may be epitaxially deposited on the first epitaxial layer 31 as described above but eliminating the iron, thus forming a monocrystalline wafer having two layers of low resistivity GaAs contiguous with but electrically separated by a layer 31 of semi-insulating GaAs. Devices formed in GaAs of the low resistivity layers 21 and 32 are electrically separated by the semi-insulating layer 31. It will be recognized that various other combinations of low resistivity and high resistivity epitaxial deposits can be used to fabricate various networks within a single wafer of monocrystalline material.

Although the invention has been described with specific reference to forming epitaxial deposits of semi-insulating gallium arsenide, it will be noted that ternary and quaternary alloys of other III-V compounds can also be formed in accordance with the invention through slight modifications of the apparatus and deposition procedure.

EXAMPLE II

A procedure similar to that of Example I was used to deposit iron-doped epitaxial Ga(As, P). After the iron was converted as described in Example I, the reactor was cooled, flushed with helium and a monocrystalline wafer of GaAs 21 placed on substrate holder 22. The reactor was closed and flushed with hydrogen. The furnaces were activated to produce temperatures of 950° C., 950° C. and 775° C. in the iron, feed and substrate zones respectively. A gaseous mixture of about 1% PCl_3 and 1% AsCl_3 in hydrogen was passed through feed tube 14 at a rate of about 100 cc./min. The flow of AsCl_3 in H_2 through feed tube 13 was about 30 cc./min. Under these conditions, an iron-doped epitaxial layer of $\text{GaAs}_{0.31}\text{P}_{0.69}$ was deposited on substrate 21 at a rate of about 0.04 microns/min. The epitaxial layer was examined and found to be P-type with a resistivity of 2×10^5 ohm-cm. at room temperature. The epitaxial layer was monocrystalline and uniform in composition and conductivity.

Monocrystalline epitaxial layers of Ga(As, P) ranging from $\text{GaAs}_{0.98}\text{P}_{0.02}$ to $\text{GaAs}_{0.3}\text{P}_{0.7}$ have deposited on various semiconductor substrates by the process described in Example II. All deposits were doped with iron using the iron arsenide as described and were found to have resistivities of 10^9 ohm-cm. or higher at room temperature. The layers having the higher phosphorous content were found to have higher resistivities.

Although the invention has been described with specific reference to forming semi-insulating layers of GaAs and Ga(As, P), it will be understood that epitaxial layers of other Group III-V compounds such as the arsenides, phosphides and antimonides of aluminum, gallium and indium as well as ternary and quaternary compounds and alloys of the same may also be doped to high resistivity with iron in accordance with this invention. It will be noted that since iron is a deep acceptor in Group III-V compounds, higher resistivities are attained with high bandgap materials than with low bandgap materials.

It is to be understood that the above-described embodiments of the invention are merely illustrative of the principles of the invention. The apparatus shown and described may be modified to introduce a plurality of volatile Group V elements or compounds to produce epitaxial ternary and quaternary III-V deposits. Numerous other arrangements and modifications may be devised by those skilled in the art without departing from the spirit and scope of the invention as defined by the appended claims.

What is claimed is:

1. The method of doping epitaxially formed deposits of Group III-V materials with iron wherein said Group III-V materials are formed by reacting a gaseous mixture comprising hydrogen, at least one Group V element or volatile compound of a Group V element, and at least one Group III element or volatile compound of a Group III element in a reaction chamber, comprising the step of introducing iron arsenide vapors into said reaction chamber during the formation of said deposits of Group III-V materials.

2. The method of claim 1 wherein said iron arsenide is introduced into said reaction chamber in a gaseous mixture produced by passing a carrier gas over iron arsenide maintained at a temperature between about 900°C . and 950°C .

3. The method of claim 2 wherein said carrier gas is a gaseous mixture comprising hydrogen and arsenic trichloride.

4. The method of making epitaxial deposits of high resistivity Group III-V compound materials on a substrate comprising the steps of:

(a) reacting a gaseous mixture of hydrogen and at least one Group V element or volatile Group V compound with a gaseous mixture of hydrogen and at least one Group III halide within a reaction chamber, and

(b) introducing iron arsenide vapors into said reaction chamber whereby a Group III-V compound doped with iron is deposited.

5. The method of claim 4 wherein said high resistivity Group III-V compound is gallium arsenide, said at least one Group V element or volatile Group V compound is arsenic or a volatile arsenic compound, and said at least one Group III halide is a gallium halide.

6. The method of claim 4, wherein said high resistivity Group III-V compound is Ga(As, P), said at least one Group V element or volatile Group V compound is a mixture of PCl_3 and AsCl_3 , and said at least one Group III halide is a gallium halide.

7. In the process of making epitaxial deposits of Group III-V materials on a substrate wherein a gaseous mixture comprising hydrogen and at least one Group V element or volatile Group V compound is mixed with a gaseous mixture comprising hydrogen and at least one Group III halide in a reaction chamber to produce a monocrystalline deposit of Group III-V material, the method of doping said monocrystalline deposit with iron comprising the steps of:

(a) reacting iron with arsenic to form iron arsenide, and

(b) forming iron arsenide vapors and introducing said iron arsenide vapors into said reaction chamber during the formation of said monocrystalline deposit.

8. The method of claim 7, wherein said iron arsenide is introduced into said reaction chamber in a gaseous stream produced by passing a mixture comprising hydrogen and arsenic trichloride over iron arsenide maintained at a temperature between about 900°C . and 950°C .

9. The method of making epitaxial deposits of high resistivity gallium arsenide on a substrate comprising the steps of:

(a) passing a gaseous mixture comprising AsCl_3 and hydrogen over iron maintained at a temperature of about 950°C . in a reaction vessel thereby producing iron arsenide,

(b) passing a gaseous mixture comprising AsCl_3 and hydrogen over a source of gallium maintained at a temperature of about 950°C ., thereby producing a first reactant mixture comprising hydrogen, arsenic halides, arsenic and gallium halides,

(c) passing a gaseous mixture of hydrogen and AsCl_3 over said iron arsenide maintained at a temperature of about 950°C ., thereby producing a second reactant mixture comprising hydrogen, arsenic halides, arsenic and iron arsenide, and

(d) mixing said first reactant mixture with said second reactant mixture in a decreasing temperature gradient.

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U.S. Cl. X.R.

117—106; 148—174; 252—62.3