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PATENT SPECIFICATION

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DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Method for making Graded Composition Mixed Compound Semiconductor Materials

We, TEXAS INSTRUMENTS INCORPORATED, a Corporation organised according to the laws of the State of Delaware, United States of America, of 13500 North Central Expressway, Dallas, Texas, 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 compound semiconductor materials, and particularly to the vapor phase growth of mixed composition compound semiconductors and graded composition compound semiconductor materials.

Semiconductor materials have become increasingly important in the field of electronics because of their usefulness in fabricating semiconductor and thermoelectric devices in extremely minute circuits. Certain properties of semiconductor materials also permit the construction of unique devices which are not possible of construction with conventional vacuum tube technology.

In the prior art, the usual semiconductor materials for fabricating devices are crystals of certain elements contained in Group IV of the Periodic Table of Elements, specifically, germanium and silicon. Experience has shown, however, that silicon devices are somewhat limited in frequency response but allow operation at temperatures up to 200°C, whereas germanium devices have relatively good frequency response but cannot operate above 85°C.

In the search for other semiconductor materials, investigators discovered that some binary and ternary compounds exhibited semiconductor properties. Some of these compound semiconductors, particularly those which contain one element from Group III and one element from Group V of the Periodic Table,

have been disclosed in U.S. Patent 2,798,989, British Patent Specification No. 719,873.

Furthermore, various characteristics of a semiconductor material, such as energy gap, lifetime of minority carriers, and electron mobility, greatly affect the utility of a device made from such material. Because of this fact, it would be desirable if various properties of certain semiconductor materials could be combined. For example, it would be desirable in solar cells to have various layers of semiconductor material with different energy gaps.

Recent advances in the semiconductor art, particularly in the areas of compound semiconductor lasers and compound semiconductor integrated circuits, have stimulated workers to develop methods of producing mixed composition compound semiconductor materials. By a mixed composition is meant a compound in which more than one element from a particular group in the Periodic Table are compounded with one or more elements from another group in the Periodic Table while maintaining stoichiometry with respect to periodic group. For example, a mixed composition compound semiconductor compounded from Groups III and V (of the Periodic Table by Mendeleef) may be represented by the general formula



Where

A, B, and C represent elements from Group IIIA;

D, E, and F represent elements from Group VA;

$a+b+c=1$, and

$d+e+f=1$,

where each lower case subscript represents the fractional number of atoms of the immediately preceding element present in a single molecule of the material represented by the general formula.

A typical example of such mixed composition compound semiconductor material is the Group III—V compound $\text{GaAs}_x\text{P}_{(1-x)}$. It will be understood that the expression $\text{GaAs}_x\text{P}_{(1-x)}$ is used herein to describe a compound wherein gallium (Ga) is combined with arsenic (As) and phosphorus (P), the number of atoms of Ga being equal to the number of atoms of As and P combined. Thus since Group III elements combine with Group V elements in a ratio of 1:1, the subscript x in the above expression is used to denote the fractional number of atoms of As which is present in a single molecule of $\text{GaAs}_x\text{P}_{(1-x)}$. Among the advantages of this material is that it has an energy gap between that of gallium arsenide (GaAs) and gallium phosphide (GaP). By the proper selection of the value of x in the above formula, a semiconductor material may be produced having any desired energy gap between the values of 1.38 eV and 2.24 eV, which are the energy gap values for GaAs and GaP, respectively.

Heretofore, processes for the production of mixed composition compound semiconductor material involved either the vapor transport or re-melt and re-growth of a physical mixture of two binary compound semiconductor materials. Thus if a ternary compound of $\text{GaAs}_x\text{P}_{(1-x)}$ was desired, it was necessary to first obtain GaAs and GaP as binary compound semiconductor materials, form a physical mixture of the composition desired by mixing portions of GaAs and GaP in a suitable powder or chunk form, and then form the ternary compound by either a suitable vapor transport reaction process or by melting the mixture and causing it to reform as a ternary compound.

One of the major disadvantages of the above processes is that the binary compounds used in the mixture, particularly the phosphides, are often difficult to produce and when used in binary form in the melting and re-growth process require excessively high vapor pressures of the volatile elements. Furthermore, it is difficult to mix granulated or powdered compounds and maintain the high purity of materials required for semiconductor purposes. Another important disadvantage is that the composition of the ternary product is determined by the mixture of binary compounds from which it is formed, and ordinarily cannot be varied during the growth of the ternary product.

In accordance with the present invention there is provided a method of producing a mixed composition compound semiconductor upon a substrate from the elements in Group III—V according to the table of Mendeleef, wherein the mixed composition semiconductor material has the general formula



each of a, b, c, d, e and f range from zero

to one and $a+b+c=1$ and $d+e+f=1$. The method comprises the steps of: placing a supply of at least one of the highly pure Group III elements Al, Ga, or In in a first part of a reaction vessel, and providing a substrate in a second part of the reaction vessel spaced apart from the first part of the reaction vessel. A stream including at least one halide of the Group V elements P, As, or Sb is injected into the first part of the vessel, and the supply of material in the first part of the reaction vessel is heated to a temperature sufficient to cause a reaction between the said supply and the constituents of the injected stream. The said injected stream includes halides of at least two of the said Group V elements when only one of the said Group III elements is placed in the first part of the vessel, when only one halide of the said Group V elements is included in the said injected stream, at least two of the said Group III elements are placed in the first part of the reaction vessel. The reactant products are transported from the first part to the second part of the vessel, with the substrate maintained at a temperature sufficient to cause a deposit of a predetermined mixed composition compound of the said Group III and V elements to be formed on the substrate. Preferably the substrate is maintained at a temperature lower than the supply material in the first part of the reaction vessel.

A method according to the invention is advantageous in that it makes possible the production of mixed composition compound semiconductor materials at atmospheric pressure and in a single operation, without the necessity of first producing intermediate binary compounds. By use of the invention, semiconductor materials of different properties can be formed and combined in a single monocrystalline body, monocrystalline semiconductor wafers comprised of layers of different semiconductor materials can be produced and regions of different electrical properties can be formed in a monocrystalline semiconductor wafer.

Another advantage of the invention is that by its use, mixed composition compound semiconductor materials can be produced having ternary product composition which can be varied as desired to form monocrystalline semiconductor material in which the composition is varied with thickness of the material.

By way of example, the invention will be described in greater detail with reference to the accompanying drawings in which:—

Figure 1 is an elevational view partially in section of apparatus suitable for the vapor phase reaction and epitaxial deposition of mixed composition compound semiconductor material of the general formula $\text{AD}_x\text{E}_{(1-x)}$, where A represents an element from Group III and D and E represent elements from Group V;

Figure 2 is an elevational view partially in



table

section of apparatus suitable for the vapor phase reaction and epitaxial deposition of mixed composition compound semiconductor material of the general formulae $A_yB_{(1-y)}D$ and $A_yB_{(1-y)}D_xE_{(1-x)}$, where A and B represent elements from Group III, D and E represent elements from Group V, y represents the fractional value of A, and x represents the fractional value of D as described in reference to Figure 1;

Figure 3 is a rectilinear plot of experimentally observed values of x versus the mole ratio of $AsCl_3$ to PCl_3 in the formation of $GaAs_xP_{(1-x)}$ in accordance with the invention; and

Figure 4 is a sectional view of a wafer upon which has been formed epitaxial deposits of ternary compounds in accordance with the invention.

Dimensions of certain parts as shown in the drawings have been modified and/or exaggerated for the purpose of clarity of illustration.

Apparatus suitable for the production of a mixed composition compound semiconductor material of the general formula $AD_xE_{(1-x)}$ is shown in Figure 1. The apparatus comprises an elongated quartz reaction vessel 10 having two inlets 11 and 12 and an exhaust 31. A constriction 13 is provided within the vessel 10 which contains the Group III feed material 14, which may be gallium, aluminum, or indium. The constriction 13 is so constructed as to cause gas entering through inlet 11 to contact the feed material 14 as it flows out of the constriction through opening 13a. As the gas passes over the feed material 14, vapors of said feed material are swept out of the constriction 13 into the reaction vessel cavity.

A carrier gas, for example, hydrogen, is admitted to the apparatus through four valves 16, 22, 28, and 35. The carrier entering through valve 16 passes through a flow meter 17 and tube 18, which has its open end submerged in a liquid halide 19 of a Group V element, for example, PCl_3 . The liquid halide 19 is contained within a closed vessel, or bubbler, 20. The bubbler is only partially filled to leave a vapor-containing space above the liquid. The gas passing through tube 18 is admitted below the surface of the liquid 19 and near the bottom of the bubbler 20. Gas so admitted rises to the surface of the liquid in small bubbles and thus becomes saturated with vapor of the liquid 19. The saturated gas leaves the bubbler 20 by way of an exit tube 21 feeding into a mixing line 15. Likewise, the carrier entering through valve 22 passes through flow meter 23 and tube 24 to bubbler 26 through a liquid halide 25 of another Group V element, for example, $AsCl_3$. The carrier gas, saturated with vapor of liquid 25, leaves the bubbler 26 by way of exit tube 27 which also feeds into the mixing line 15. Carrier gas admitted by valve

28 passes through flow meters 29 and tube 30 into line 15 to assure mixing of the vapors and provide further dilution.

Thus a mixture of carrier gas and vapors of the two Group V halides is introduced into the reaction vessel 10 through inlet 11. The reaction vessel 10 is positioned within an appropriate furnace having two separately controlled temperature zones shown at 32 and 33. The vapors react with the feed material 14, forming the ternary semiconductor material of mixed composition on the surface of a substrate wafer 34 positioned in the cooler zone 33. Reaction by-products are exhausted through the exhaust 31.

Additional carrier gas, for example, hydrogen, passing through valve 35, flow meter 36, and tube 37 is introduced into the reaction chamber by way of inlet 12 to assure complete reaction and assist the flow of reactants toward the substrate. Temperature controlling devices 38 and 39 are disposed about the bubblers 20 and 26 to provide an additional control over the amount of Group V halides admitted into the reaction vessel 10.

To flush atmospheric gases such as oxygen and water vapor from the reaction vessel 10, an inert gas such as helium may be admitted through valve 40 before the reaction is begun.

Operation of the apparatus will be readily understood from the following typical examples.

EXAMPLE I.

A GaAs substrate 34 was placed in a reaction vessel, such as vessel 10, as shown in Figure 1. High purity gallium was used as the Group III feed material 14. The reaction vessel was flushed with dry helium, admitted through valve 40, and the individually controlled furnace zones 32 and 33 were activated to raise the temperatures of the feed material 14 and the substrate 34 to $950^\circ C$ and $790^\circ C$, respectively. The first bubbler 20 was filled with $AsCl_3$ and maintained at room temperature. The second bubbler, containing PCl_3 , was likewise maintained at room temperature throughout the deposition run. When the substrate 34 and the feed material 14 reached the designated temperatures, the helium flush was stopped and purified hydrogen was introduced through inlet 12 at a rate of $20 \text{ cm}^3/\text{minute}$. Hydrogen was passed through the $AsCl_3$ in bubbler 20 at the rate of $30 \text{ cm}^3/\text{minute}$ and through the PCl_3 in bubbler 26 at a rate of $2 \text{ cm}^3/\text{minute}$. Additional hydrogen was admitted into the mixing line 15 from valve 35 at a rate of $58 \text{ cm}^3/\text{minute}$. $GaAs_{0.6}P_{0.4}$ was epitaxially deposited on the surface of the GaAs substrate wafer 34 at the rate of 16 microns per hour. The deposit was a monocrystalline extension of the crystal lattice of substrate wafer 34, thus the resulting product was a single monocrystalline wafer comprised of two contiguous regions, GaAs and $GaAs_{0.6}P_{0.4}$.



EXAMPLE II.

An N-type GaAs wafer 34 was placed in the reaction vessel 10 as shown in Figure 1. High purity gallium was used as the feed material 14. The reaction vessel was flushed with dry helium and the individually controlled furnace zones 32 and 33 actuated to raise the temperature of the feed material 14 to 915°C and the substrate wafer 34 to 790°C. The first bubbler 20 was filled with AsCl₃ and maintained at room temperature. The second bubbler containing PCl₃ was also maintained at room temperature. When the substrate and the feed material reached the designated temperatures, the helium flush was stopped and hydrogen passing through valve 35 was admitted into the reaction vessel 10 through inlet 12 at the rate of 20 cm³/minute. Hydrogen was passed through the AsCl₃ in bubbler 20 at the rate of 30 cm³/minute and through the PCl₃ in bubbler 26 at the rate of 2 cm³/minute. During the first 20 minute deposition period, the hydrogen flow rates were gradually changed as follows: the flow rate through the AsCl₃ in bubbler 20 was gradually reduced from 30 cm³/minute to zero. The flow rate through the PCl₃ in bubbler 26 was simultaneously increased from 2 to 7 cm³/minute. Additional hydrogen was introduced through mixing line 15 initially at 58 cm³/minute and was gradually increased to 101 cm³/minute. The changes were made gradually and simultaneously. At the end of the 20 minute period these conditions were maintained for an additional 4 hours. All hydrogen was then stopped and dry helium through valve 40 flushed through the reaction vessel 10 while the substrate 34 was allowed to cool to room temperature.

The material formed during the first 20 minutes was monocrystalline material in which the composition varied with depth from GaAs_{0.6}P_{0.4} at the interface adjoining the GaAs substrate to GaP. The layer was approximately 4 microns thick. The material deposited during the last 4 hours of the deposition run was GaP since no AsCl₃ was admitted to the reaction chamber.

EXAMPLE III.

An N-type GaAs wafer 34 was placed in the reaction vessel 10 as shown in Figure 1. High purity gallium was used as the feed material 14. The bubblers 20 and 26 contained AsCl₃ and PCl₃, respectively. Dry helium admitted through valve 40 was flushed through the reaction vessel 10 and the heating elements 32 and 33 were activated to bring the temperature of the gallium 14 to 950°C and the substrate wafer 34 to 790°C. When the desired temperatures were obtained, the helium flush was stopped and purified hydrogen was admitted into the vessel 10 through inlet 12 at a rate of 20 cm³/minute. Hydrogen was passed through the AsCl₃ in bubbler 20 at a rate of 30 cm³/minute and through the PCl₃ in bubbler

26 at a rate of 2 cm³/minute. Additional hydrogen was admitted into the mixing line 15 at a rate of 58 cm³/minute.

These conditions were maintained for 90 minutes. The flow rate through bubbler 20 was then abruptly reduced from 30 to 9 cm³/minute and the flow rate through bubbler 26 simultaneously increased from 2 to 4 cm³/minute. The additional hydrogen being admitted into the mixing line 15 was increased from 58 to 93 cm³/minute. These conditions were maintained for 120 minutes. The flow of hydrogen through bubbler 20 was then stopped and the flow through bubbler 26 again increased from 4 to 9 cm³/minute. These conditions were maintained for 90 minutes. All hydrogen was then stopped and dry helium through valve 40 flushed through the reaction vessel 10 while the substrate 34 was allowed to cool to room temperature. Upon examination, the GaAs substrate 34 was found to have an epitaxial layer of GaAs_{0.6}P_{0.4} 47 microns thick, another epitaxial layer of GaAs_{0.18}P_{0.82} 60 microns thick, and a third epitaxial layer of GaP 52 microns thick.

The mixed composition semiconductor material formed by the above process was monocrystalline and was epitaxially grown as an extension of the crystal structure of the substrate wafer. It will be understood that the resultant material and the original substrate wafer comprise a single monocrystalline wafer, although the composition of the material varies from GaAs (substrate 34) to GaP.

The resultant layered structure is illustrated in Figure 4. The substrate wafer is shown at 34, upon which is epitaxially deposited a layer 90 of GaAs_{0.6}P_{0.4}. Layer 90 is of the same crystal orientation as wafer 34 and is formed as a continuous extension of the crystal lattice. Adjoining the GaAs_{0.6}P_{0.4} layer 90 is a GaAs_{0.18}P_{0.82} layer 91, which is also a continuous extension of the original crystal lattice of wafer 34. The top layer 92 is an epitaxial layer of GaP deposited on the surface of layer 91. Thus the original crystal orientation of wafer 34 is propagated by the growth of mixed composition material on the surface thereof, producing a single monocrystalline mass or wafer comprised of layers of different semiconductor materials.

It has been found that the important variables which control the composition of the product material are composition of the feed material and the ratio of AsCl₃ to PCl₃ introduced into the apparatus. With respect to composition of the feed material, the complete composition range of GaAs_xP_(1-x) for values of x from zero to unity has been epitaxially grown on GaAs substrates using pure gallium as the feed material in accordance with the invention, but if gallium arsenide is used as the feed material, which use does not form part of the invention, the composition range of the product material is limited as hereinafter ex-



plained. The ratio of AsCl_3 to PCl_3 may be controllably varied by any of several means. For abrupt changes in the ratio of AsCl_3 to PCl_3 , for example, a ~~single~~ increase in the flow rate of hydrogen through the appropriate bubbler by appropriate adjustment of valves 16 and 22 will result in an increase in the amount of vapor of that particular halide being introduced into the reaction vessel 10, and consequently change the composition of the product material. A gradual change in the temperature of the appropriate bubbler will also change the amount of halide vapor introduced into the reaction chamber.

The vapor pressure of the halide liquid (and the concentration of halide in the gas above the halide liquid) varies with temperature. By introducing the carrier gas below the surface of the liquid in the bubblers, the incoming gas displaces the vapor-containing gas in the bubblers. The vapor-containing gas is then introduced into the reaction vessel. Thus the flow rate of the carrier through the bubbler and the temperature of the bubbler both affect the amount of halide vapor introduced into the reaction vessel. The flow rate and the temperature of each bubbler may be individually controlled. A gradual change in the temperature of one or both of the bubblers is particularly useful in producing epitaxial layers in which the composition of the Group V elements varies with depth. Furthermore, the desired temperature change can be automatically controlled by a suitable temperature programming.

Figure 3 illustrates the effect of the mole ratio of AsCl_3 to PCl_3 introduced into the system on the product composition for Ga and GaAs feed materials. The data shown in Figure 3 is a rectilinear plot of the value of

x in material of the form $\text{GaAs}_x\text{P}_{(1-x)}$ produced in the apparatus of Figure 1 versus the mole ratio

$$\frac{\text{PCl}_3}{\text{PCl}_3 + \text{AsCl}_3}$$

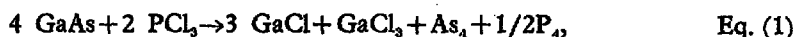
injected into the reaction vessel 10. As can be seen from the figure, the complete composition range has been synthesized using Ga feed material. However, $\text{GaAs}_{0.67}\text{P}_{0.33}$ was the highest phosphorous composition produced using GaAs feed material. This material was produced when the mole ratio

$$\frac{\text{PCl}_3}{\text{PCl}_3 + \text{AsCl}_3}$$

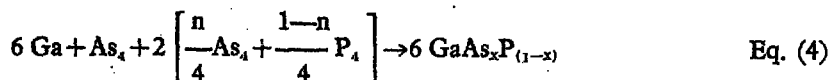
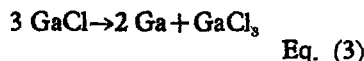
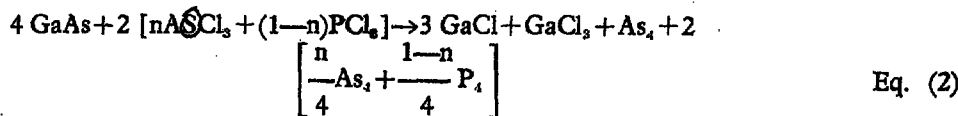
= 1, or simply stated, when only PCl_3 was injected into the reaction vessel 10.

The following characterizes the probable chemical reactions involved in the process of the invention. The reaction between Ga and a halide source will form mono-, di-, and trihalides. The di-halide is thought to be a loosely associated $\text{Ga}(\text{GaCl}_2)$ complex and probably does not exist in the gaseous state. The gallium feed data in Figure 3 indicates that the composition of $\text{GaAs}_x\text{P}_{(1-x)}$ formed is roughly proportional to the mole ratio of arsenic to phosphorus present in the reaction vessel.

The GaAs feed data in Figure 3 have shown that the reaction between PCl_3 and GaAs produces $\text{GaAs}_{0.67}\text{P}_{0.33}$. This indicates that the ratio of arsenic to phosphorus present in the deposition zone must be two to one. Equation (1),



gives such a ratio. Assuming that 3 moles of one can propose the following over-all series of reactions:



$$\text{where } x = \frac{2+n}{3}$$

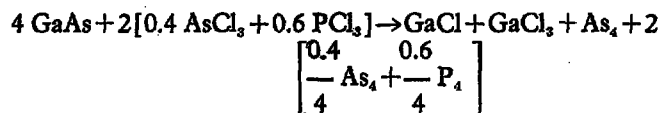
First, the GaAs reacts with the AsCl_3 and PCl_3 (Eq. 2). In the decreasing temperature gradient the GaCl disproportionates (Eq. 3),

forming gallium which is then able to react (Eq. 4) with the arsenic and phosphorus available in the gas phase. Thus, the mole ratio of PCl_3 to AsCl_3 necessary to form a desired composition of $\text{GaAs}_x\text{P}_{(1-x)}$ using GaAs feed material may be determined by the substitution

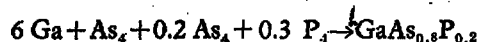
of a predetermined value of X in the above series of equations. For example, if the product material to be produced is $\text{GaAs}_{0.8}\text{P}_{0.2}$, the

value of $x=0.8$, since $x=\frac{2+n}{3}$, $n=0.4$. By

substituting 0.4 for n in the above series of equations:



Eq. (2a)



Eq. (4a)

Thus, the mole ratio of

$$\frac{\text{PCl}_3}{\text{PCl}_3 + \text{AsCl}_3}$$

must be 0.6.

The reaction shown in Equation 2 is complicated by the fact that AsCl_3 and PCl_3 are reduced by hydrogen at elevated temperatures.

This would seem to indicate that while the over-all reaction proposed in Equation (2) describes our results, the mechanism may involve HCl as an intermediate.

The reactions with gallium feed material are similar to the reaction with gallium arsenide feed material except that in the former

AsCl_3 is the only arsenic source. Moreover, it will be understood that indium (In) or aluminum (Al) may be substituted for gallium, and antimony (Sb) may be substituted for either As or P in the reactions described.

The growth rate of the ternary product is primarily controlled by the temperature of the substrate and the total flow rate of the reactants. In the preferred mode of operation, the total flow rate through a reaction vessel of about one inch in diameter is from about 100 $\text{cm}^3/\text{minute}$ to about 150 $\text{cm}^3/\text{minute}$. Very high flow rates tend to cause etching of the substrate, in which event epitaxial growth does not occur. Typical growth rates of $\text{GaAs}_x\text{P}_{(1-x)}$ observed at various substrate temperatures are shown in Table I.



TABLE I

Substrate	Unit No.	Substrate Temperature	Feed Material	Feed Material Temperature	H ₂ Flow Through PCl ₃ (cm ³ /minute)	H ₂ Flow Through AsCl ₃ (cm ³ /minute)	Growth Rate (Microns/Hour)	Product Composition
GaAs	1	835° C.	Ga	950° C.	4	20	0.0	
GaAs	2	825° C.	Ga	950° C.	4	20	3.3	GaAs _{0.87} P _{0.88}
GaAs	3	815° C.	Ga	950° C.	4	20	50.0	GaAs _{0.37} P _{0.68}
GaAs	4	805° C.	Ga	950° C.	4	20	17.0	GaAs _{0.37} P _{0.68}
GaAs	5	795° C.	Ga	950° C.	4	20	14.0	GaAs _{0.37} P _{0.68}
GaAs	6	785° C.	Ga	950° C.	4	20	11.0	GaAs _{0.37} P _{0.68}

Total flow through reaction tube of one inch diameter was 134 cm³/minute.



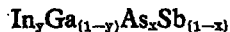
The above process, although in terms of $\text{GaAs}_x\text{P}_{(1-x)}$, is intended as illustrative and not limitative. It is to be understood that by using aluminum or indium as the feed material 14 in the apparatus of Figure 1, various compositions of the mixed compound semiconductor materials $\text{AlAs}_x\text{P}_{(1-x)}$ and $\text{InAs}_x\text{P}_{(1-x)}$ may be produced by the same process. Moreover, halides of antimony, for example SbCl_3 or SbCl_5 , may be used in either of the bubblers 20 and 26 to produce such compounds as $\text{InSb}_x\text{As}_{(1-x)}$, $\text{GaAs}_x\text{Sb}_{(1-x)}$ and $\text{AlP}_x\text{Sb}_{(1-x)}$. It will be understood that the principles of the above-described process may be applied to produce any desired composition of ternary compound semiconductor material comprised of one of the Group III elements, Al, Ga, and In, and more than one of the Group V elements, P, As, and Sb. If desired, halides of As, P, and Sb may all be introduced into the reaction vessel to produce a mixed composition of one Group III element and three Group V elements. Furthermore, since the gaseous reactants can be varied or substituted during the production process, wafers may be produced wherein the composition of the material changes with the thickness of the material. By introducing selected conductivity-affecting or type-determining impurities in the gas stream in predetermined amounts, wafers may be produced having P-N junctions therein. Thus, for example, the collector, base, and emitter regions of a transistor may be epitaxially grown on a semiconductor substrate. It will be appreciated that such junctions can be formed at any stage in the production process.

Apparatus suitable for the production of mixed composition compound semiconductors of the general formulae $\text{A}_y\text{B}_{(1-y)}\text{D}$ and $\text{A}_y\text{B}_{(1-y)}\text{D}_x\text{E}_{(1-x)}$ in accordance with the invention is shown in Figure 2. The apparatus comprises a reaction vessel 50 having two reaction chambers 51 and 52 and a deposition or growth chamber 53. Positioned within the reaction chamber 51 is a constriction 54 having an opening 54a and containing a Group III feed material 55, for example indium. An inlet 56 is provided to admit gas which flows through the constriction 54 and over the feed material 55 before entering the reaction chamber 51. Likewise, positioned within the second reaction chamber 52 is a constriction 63 containing another Group III feed material, for example gallium. A substrate wafer 65 is positioned in the deposition chamber 53. A carrier gas, for example purified hydrogen, is admitted into the apparatus through four valves 57, 67, 74, and 78. Carrier gas passing through valve 57 and flow meter 58 enters a bubbler 59 below the level of a liquid halide 60 of a Group V element, for example AsCl_3 . The carrier, saturated with vapor of the liquid, flows through tube 61 and enters the constriction in reaction chamber 51 through inlet 56. If desired, dilu-

tion of the vapor in tube 61 may be provided by an additional hydrogen input as described with reference to Figure 1. The carrier gas passing through valve 67 and flow meter 68 enters a second bubbler 69 below the level of the liquid halide 70 of a Group V element contained therein. Carrier gas saturated with vapors of the halide flows from the bubbler 69 through tube 71 and enters the constriction 63 in the second reaction chamber 52 through inlet 66. If a ternary compound of the formula $\text{A}_y\text{B}_{(1-y)}\text{D}$ is to be produced, the Group V halide will be the same in both bubblers 59 and 69. The bubblers are provided with temperature controlling devices 72 and 73 to control the amount of halide in the vapor, and consequently the amount of the Group V element available for reaction.

The three chambers of the reaction vessel 50 are positioned within a suitable furnace having three separately controlled temperature zones 82, 83, and 84, such that the reaction chambers 51 and 52 may be individually maintained at different temperatures while the deposition chamber 53 may be maintained at yet a third temperature. The vapors enter the reaction vessel through inlets 56 and 66 and react with the Group III feed materials 55 and 64 to form a ternary product which is epitaxially deposited on the substrate 65 in the deposition chamber. The reaction by-products are exhausted through outlet 81. Additional hydrogen passing through valve 74, flow meter 75, and tube 76 enters the reaction chamber 51 through inlet 77 to assure complete reaction and to assist the flow of reactants to the deposition chamber. Likewise, additional hydrogen passing through valve 78, flow meter 79, and tube 80 enters the second reaction chamber 52 through inlet 62.

Quarternary compounds of the formula $\text{A}_y\text{B}_{(1-y)}\text{D}_x\text{E}_{(1-x)}$ may also be produced with the apparatus shown in Figure 2. For example, if the compound semiconductor



is to be produced, indium and gallium may be placed in constrictions 54 and 63; and halides of arsenic and antimony, for example AsCl_3 and SbCl_5 , placed in the bubblers 59 and 69. Similarly, other quarternary compounds of the Group III and Group V elements may be produced by the proper selection of the desired Group III elements and Group V halides. If desired, mixed compositions of any combination having at least one element from the Group III elements aluminum, gallium, and indium, and at least one element from the Group V elements phosphorus, arsenic, and antimony may be produced in the apparatus of Figure 2 in accordance with the invention by placing the appropriate reactant materials in the proper part of the apparatus.

constriction

70

75

80

85

90

95

100

105

110

115

120

125



Operation of the apparatus of Figure 2 is basically the same as for the apparatus of Figure 1. For example, the ternary mixed composition compound semiconductor

5 $\text{In}_y\text{Ga}_{(1-y)}\text{As}$

may be produced by placing pure indium 55 in constriction 54, pure gallium 64 in constriction 63, and AsCl_3 in both bubblers 59 and 69. A suitable substrate 65 having a compatible unit cell size, such as GaAs or germanium for example, is placed in the deposition chamber 53. Dry helium is admitted through valves 85 and 86 and flushed through the reaction vessel. Furnace zones 82, 83, and 84 are activated to bring the temperature of the deposition chamber 53 to about 750°C , the indium reaction chamber 51 to about 900°C , and the gallium reaction chamber 52 to about 900°C . It will be understood that the temperatures of each of the chambers 51, 52, and 53 may be advantageously selected to provide optimum reaction conditions for the particular reactant contained therein and may vary from 450°C to 1100°C in the deposition chamber 53 and from 600°C to 1300°C in the reaction chambers 51 and 52. The preferred temperature range for chambers 51 and 52 is from 850°C to 1050°C . The preferred temperature range for the deposition chamber 53 is from 750°C to 950°C . It is to be noted that the limits of these temperature ranges are not critical and that useful results can be obtained dependent on operating conditions, outside these preferred ranges.

When the desired temperatures are achieved, the helium flush is stopped and hydrogen admitted to the reaction chambers through inlets 62 and 77. Hydrogen is then admitted through valve 67 and flow meter 68 and bubbled through the liquid AsCl_3 in bubbler 69. The hydrogen carrying AsCl_3 vapors then flows through tube 71 and is introduced into the gallium reaction chamber 52 at inlet 66. Likewise, hydrogen passing through valve 57, flow meter 58, bubbler 59, and tube 61 carries AsCl_3 vapors to the indium reaction chamber 51 and is admitted through inlet 56. $\text{In}_y\text{Ga}_{(1-y)}\text{As}$ is formed and epitaxially deposited on the surface of the substrate wafer 65. Reaction by-products are exhausted through exhaust 81. The composition of the ternary product is determined by the ratio of AsCl_3 introduced into the indium reaction chamber 51 to the AsCl_3 introduced into the gallium reaction chamber 52. If no carrier gas is passed through bubbler 59, no AsCl_3 will be present to react with and transport the indium into chamber 51. Thus the product will be GaAs. Conversely, if no carrier gas is passed through bubbler 69, there will be no AsCl_3 in the gallium chamber 52 and the product will be InAs. However, by passing a controlled flow of hydrogen through both bubblers, AsCl_3 and

hydrogen are controllably admitted in the desired proportions into each of the reaction chambers 51 and 52. The resultant ternary product, $\text{In}_y\text{Ga}_{(1-y)}\text{As}$, is epitaxially deposited on the substrate wafer 65 with the value of y controlled by the ratio of the flow rates through bubblers 59 and 69. By proper control of these flow rates, the value of y may be varied from zero to one. Furthermore, the flow rates may be changed during the growth process to form layers of different composition in the same monocrystalline product. This is readily accomplished by a change in the flow rate of hydrogen through one or both of the bubblers. The composition may also be changed gradually to produce a ternary product of graded composition, that is, one in which the composition varies with the thickness of the deposit. This is most readily accomplished by gradually changing the temperature of one of the bubblers. Since the vapor pressure of the liquid Group V halide varies with temperature, the concentration of halide vapor in the space above the liquid in the bubbler varies with temperature of the bubbler. By introducing hydrogen below the liquid in the bubbler, the gas above the liquid which contains the halide vapor is displaced. Thus the temperature of the bubbler determines the concentration of halide vapor in the carrier gas.

It will be appreciated that in accordance with this invention mixed composition compounds are produced without using binary compounds. Furthermore, since the Group V constituents are provided in a halide compound, it will be understood that a third bubbler may be added to the apparatus of Figure 1 or Figure 2 to permit individually controlled introduction of each of the three elements (P, Sb, As) into the reaction vessel. Thus the amount of P, Sb, and/or As in the resultant product may be varied during the growth of the material to provide a contiguous monocrystalline product comprising layers of different semiconductor material, or layers of monocrystalline material which gradually change in composition from one binary compound to another binary compound. Furthermore, the apparatus of Figure 2 can also be used to produce material of the form $\text{AD}_x\text{E}_{(1-x)}$ by placing Group V material in one of the constrictions 54 or 63. In this case only carrier gas need be passed through the constriction containing the Group V material. It will be understood that simple changes in the mixing tube arrangement may be made to provide the combination of reactants necessary for any desired product composition without departing from the spirit and scope of this invention.

It will also be understood that the principles applicable to the apparatus of Figure 2 are equally applicable to an apparatus having three or more reaction chambers communicating to a single growth chamber wherein

the mixed composition material is deposited on a substrate.

- 5 Doping impurities may be included in the product material as grown to produce either N- or P-type material. For example, the addition of H_2S to the carrier gas results in a sulfur-doped semiconductor product. H_2S may be admitted in controlled quantities to the mixing tube in the arrangement of Figure 1 to produce N-type mixed composition compound semiconductor material. Impurities such as zinc and cadmium may be included to the Group III feed material, or may be included in suitable form in the Group V halide to produce P-type material.

WHAT WE CLAIM IS:—

1. A method of producing a mixed composition Group III—V compound semiconductor upon a substrate from the elements in Group III—V according to the Table by Mendeleef wherein the mixed composition semiconductor material has the general formula



- 25 wherein each of a, b, c, d, e, and f range from zero to one and $a+b+c=1$ and $d+e+f=1$, comprising the steps of

- (a) placing a supply of at least one of the highly pure Group III elements Al, Ga, or In in a first part of a reaction vessel,
- 30 (b) providing a substrate in a second part of the reaction vessel spaced apart from the first part of the reaction vessel,
- 35 (c) injecting a stream including at least one halide of the Group V elements P, As, or Sb into the first part of the vessel, the said stream including halides of at least two of the said Group V elements when only one of the said Group III elements is placed in the first part of the vessel, and at least two of the said Group III elements being placed in the first part of the vessel when only one halide of the said Group V elements is included in the said stream,
- 40 (d) heating the said supply in the first part of the reaction vessel to a temperature sufficient to cause a reaction between the said supply and the constituents of the injected stream,
- 45 (e) transporting the reactant products from the first part to the second part of the vessel, and
- 50 (f) maintaining the substrate at a temperature sufficient to cause a deposit of a predetermined mixed composition compound of the said Group III and V elements to be formed on the substrate.

2. A method according to claim 1, wherein the substrate is maintained at a temperature lower than the supply material in the first part of the reaction vessel.

3. A method of producing the mixed composition compound semiconductor material

$GaAs_xP_{(1-x)}$ on a substrate comprising

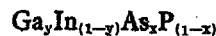
- (a) placing a supply of Ga in a first part of a reaction vessel, and a substrate in a second part of the vessel,
- (b) maintaining the Ga supply at $850^\circ C$ to $1050^\circ C$,
- (c) entraining halides of arsenic and phosphorus in a gaseous carrier,
- (d) introducing the carrier and the halides into the first part of the reaction vessel, and
- (e) maintaining a decreasing temperature gradient along the length of the reaction vessel, the temperature decreasing in the direction of gas flow and in the direction leading from the first part to the second part of the vessel thereby causing the mixed composition compound semiconductor material $GaAs_xP_{(1-x)}$ to be deposited on the substrate.

4. A modification of the method according to claim 3, wherein the compound semiconductor material produced on the substrate is $InAs_xSb_{(1-x)}$, wherein the material placed in the first part of the reaction vessel is indium, and wherein halides of antimony and arsenic are entrained in the gaseous carrier thereby causing the predetermined $InAs_xSb_{(1-x)}$ compound to be deposited on the substrate.

5. A method of producing the mixed composition compound semiconductor material $Ga_yIn_{(1-y)}As$ on a substrate, comprising:

- (a) placing a supply of indium in a first part of a reaction vessel and a supply of gallium in a second part of the reaction vessel,
- (b) providing a substrate in a third part of the vessel,
- (c) maintaining the gallium and the indium at $850^\circ C$ to $1050^\circ C$,
- (d) entraining a halide of arsenic in a gaseous carrier,
- (e) introducing the carrier and the halide into the first and second parts of the reaction vessel, and
- (f) maintaining a decreasing temperature gradient along the length of the vessel, the temperature decreasing in the direction of gas flow and in the direction leading from the first and second parts of the third part of the vessel, thereby causing the compound semiconductor material $Ga_yIn_{(1-y)}As$ to be deposited on the substrate.

6. A modification of the method according to claim 5 for producing the mixed composition compound semiconductor material



upon a substrate, in which in the said steps (d) and (e) halides of arsenic and phosphorus are entrained in separate streams of a gaseous carrier, and each of the separate halide-containing carrier streams are introduced into



the mixed composition material is deposited on a substrate.

- 5 Doping impurities may be included in the product material as grown to produce either N- or P-type material. For example, the addition of H_2S to the carrier gas results in a sulfur-doped semiconductor product. H_2S may be admitted in controlled quantities to the mixing tube in the arrangement of Figure 1 to produce N-type mixed composition compound semiconductor material. Impurities such as zinc and cadmium may be included to the Group III feed material, or may be included in suitable form in the Group V halide to produce P-type material.

WHAT WE CLAIM IS:—

1. A method of producing a mixed composition Group III—V compound semiconductor upon a substrate from the elements in Group III—V according to the Table by Mendeleef wherein the mixed composition semiconductor material has the general formula



- 25 wherein each of a, b, c, d, e, and f range from zero to one and $a+b+c=1$ and $d+e+f=1$, comprising the steps of

- (a) placing a supply of at least one of the highly pure Group III elements Al, Ga, or In in a first part of a reaction vessel, 30
(b) providing a substrate in a second part of the reaction vessel spaced apart from the first part of the reaction vessel,
(c) injecting a stream including at least one halide of the Group V elements P, As, or Sb into the first part of the vessel, the said stream including halides of at least two of the said Group V elements when only one of the said Group III elements is placed in the first part of the vessel, and at least two of the said Group III elements being placed in the first part of the vessel when only one halide of the said Group V elements is included in the said stream, 45
(d) heating the said supply in the first part of the reaction vessel to a temperature sufficient to cause a reaction between the said supply and the constituents of the injected stream, 50
(e) transporting the reactant products from the first part to the second part of the vessel, and
(f) maintaining the substrate at a temperature sufficient to cause a deposit of a predetermined mixed composition compound of the said Group III and V elements to be formed on the substrate. 55

2. A method according to claim 1, wherein the substrate is maintained at a temperature lower than the supply material in the first part of the reaction vessel.

3. A method of producing the mixed composition compound semiconductor material

$GaAs_xP_{(1-x)}$ on a substrate comprising

- (a) placing a supply of Ga in a first part of a reaction vessel, and a substrate in a second part of the vessel, 65
(b) maintaining the Ga supply at $850^\circ C$ to $1050^\circ C$, 70
(c) entraining halides of arsenic and phosphorus in a gaseous carrier,
(d) introducing the carrier and the halides into the first part of the reaction vessel, and 75
(e) maintaining a decreasing temperature gradient along the length of the reaction vessel, the temperature decreasing in the direction of gas flow and in the direction leading from the first part to the second part of the vessel thereby causing the mixed composition compound semiconductor material $GaAs_xP_{(1-x)}$ to be deposited on the substrate. 80

4. A modification of the method according to claim 3, wherein the compound semiconductor material produced on the substrate is $InAs_xSb_{(1-x)}$, wherein the material placed in the first part of the reaction vessel is indium, and wherein halides of antimony and arsenic are entrained in the gaseous carrier thereby causing the predetermined $InAs_xSb_{(1-x)}$ compound to be deposited on the substrate. 85

5. A method of producing the mixed composition compound semiconductor material $Ga_yIn_{(1-y)}As$ on a substrate, comprising: 95

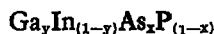
- (a) placing a supply of indium in a first part of a reaction vessel and a supply of gallium in a second part of the reaction vessel, 100
(b) providing a substrate in a third part of the vessel,
(c) maintaining the gallium and the indium at $850^\circ C$ to $1050^\circ C$,
(d) entraining a halide of arsenic in a gaseous carrier, 105
(e) introducing the carrier and the halide into the first and second parts of the reaction vessel, and
(f) maintaining a decreasing temperature gradient along the length of the vessel, the temperature decreasing in the direction of gas flow and in the direction leading from the first and second parts of the third part of the vessel, thereby causing the compound semiconductor material $Ga_yIn_{(1-y)}As$ to be deposited on the substrate. 110

6. A modification of the method according to claim 5 for producing the mixed composition compound semiconductor material 120



upon a substrate, in which in the said steps (d) and (e) halides of arsenic and phosphorus are entrained in separate streams of a gaseous carrier, and each of the separate halide-containing carrier streams are introduced into 125

respective ones of the first and second parts of the vessel, and in which the said step (f) causes a mixed composition compound



5 to deposit on the substrate.

7. A modification of the method according to claim 5 for producing the mixed composition compound semiconductor material



10 upon a substrate, in which in step (a) a supply of aluminium is placed in the first part of a reaction vessel and a supply of gallium in a second part of said reaction vessel, in which in step (d) halides of phosphorus and antimony are entrained in separate streams of a gaseous carrier, and in which the step (f) causes the compound semiconductor material $\text{Al}_y\text{Ga}_{(1-y)}\text{P}_x\text{Sb}_{(1-x)}$ to be deposited on the substrate.

20 8. A method according to claim 1 for producing a graded mixed composition compound semiconductor, in which controlled amounts of the halides of the Group V elements P, As and Sb are fed individually into the stream and are varied to cause a graded mixed composition to be deposited on the substrate, which composition varies in the direction of thickness of the deposit.

30 9. The process of claim 8, wherein the halides are chlorides selected from the group consisting of AsCl_3 , PCl_3 , SbCl_3 , and SbCl_5 .

35 10. The process of claim 8, wherein the halides are entrained in a carrier gas by passing the gas through containers of the halides.

11. The process of claim 10, wherein the

controlled amounts of the halides of Group V elements are varied by varying the flow rate of the carrier gas through the containers.

40 12. The process of claim 10, wherein the controlled amounts of the halides of Group V elements are varied by varying the temperatures of the separate supplies of halides.

45 13. A method according to claim 8, wherein a plurality of supplies of at least one of the Group III elements Al, Ga and In are placed in selected parts of the reaction vessel.

50 14. A method according to claim 3, in which the ratio of arsenic to phosphorus in the halides entrained in the gaseous carrier introduced into the first part of the reaction vessel is changed during the formation of the deposit on the substrate, thereby causing a graded mixed composition of $\text{GaAs}_x\text{P}_{(1-x)}$ to be deposited on the substrate, the value of x 55 varying in the direction of the thickness of the deposit.

60 15. A method according to claim 1, in which the substrate is a monocrystalline semiconductor of a first conductivity-type, and including the additional step of introducing conductivity-affecting impurities of a second conductivity-type into the reaction vessel, whereby there is produced a monocrystalline semiconductor body comprising the substrate of the first conductivity-type and an epitaxial deposit of the second conductivity-type thereon. 65

70 16. A substrate having a mixed composition Group III—V compound semiconductor deposited thereon by a method as defined by any one of claims 1—15.

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