

[54] VAPOR PHASE GROWTH OF GROUPS III-V COMPOUNDS BY HYDROGEN CHLORIDE TRANSPORT OF THE ELEMENTS

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[22] Filed: Dec. 19, 1973

[21] Appl. No.: 426,405

[52] U.S. Cl. 148/175; 117/106 A; 117/107.2; 117/201; 118/48; 118/49.1; 252/62.3 GA

[51] Int. Cl. H011 7/36; C23c 11/00

[58] Field of Search 148/174, 175; 117/106 A, 117/107.2, 201; 118/48, 49.1; 252/62.3 GA

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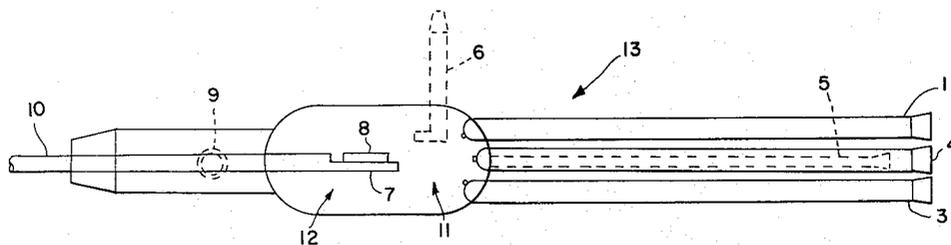
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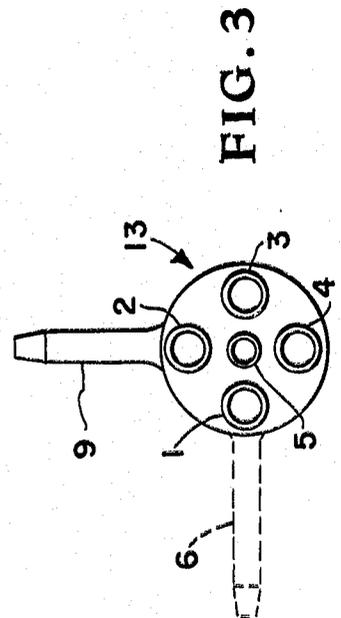
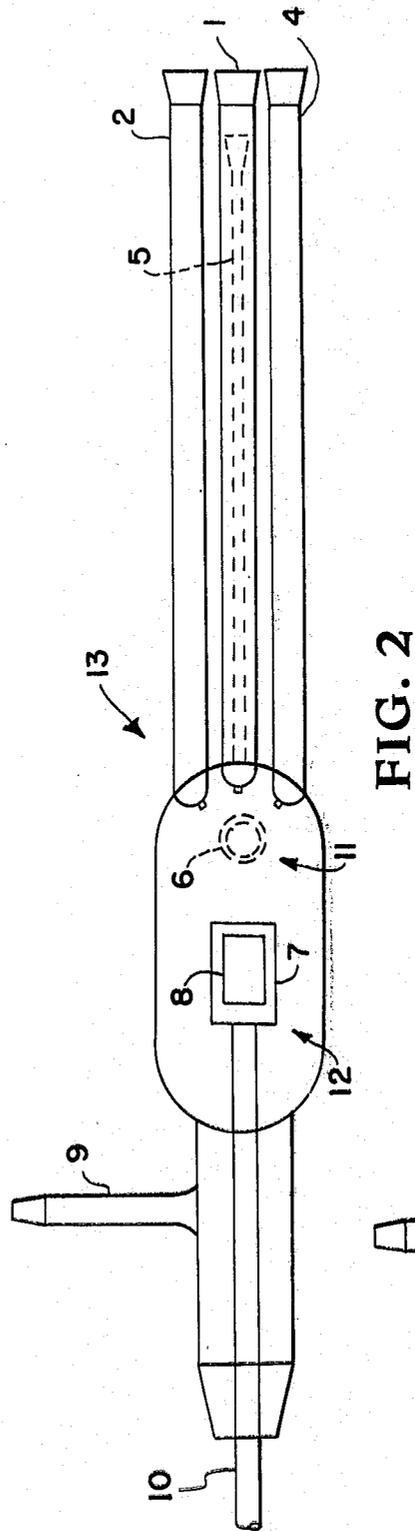
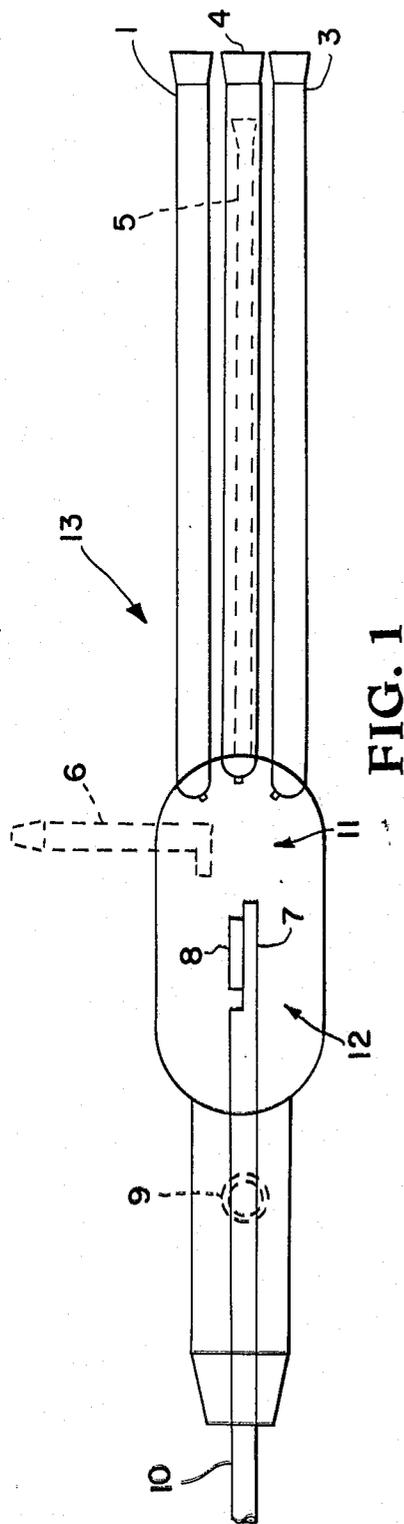
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[57] **ABSTRACT**

A method of forming binary, ternary, and quaternary compounds derived from elements of Groups III-V wherein a hydrogen chloride-hydrogen carrier gas is separately contacted with the desired elements at elevated temperatures to provide the corresponding subchlorides, which are then transported to a reaction zone for final deposition of the respective elements on a single crystal substrate derived from one or more elements of Groups III-V, with the rate of flow of the carrier gas over each element being adjusted such that the elements are deposited on the substrate in sufficient amounts to provide the desired binary, ternary, or quaternary compound.

6 Claims, 4 Drawing Figures





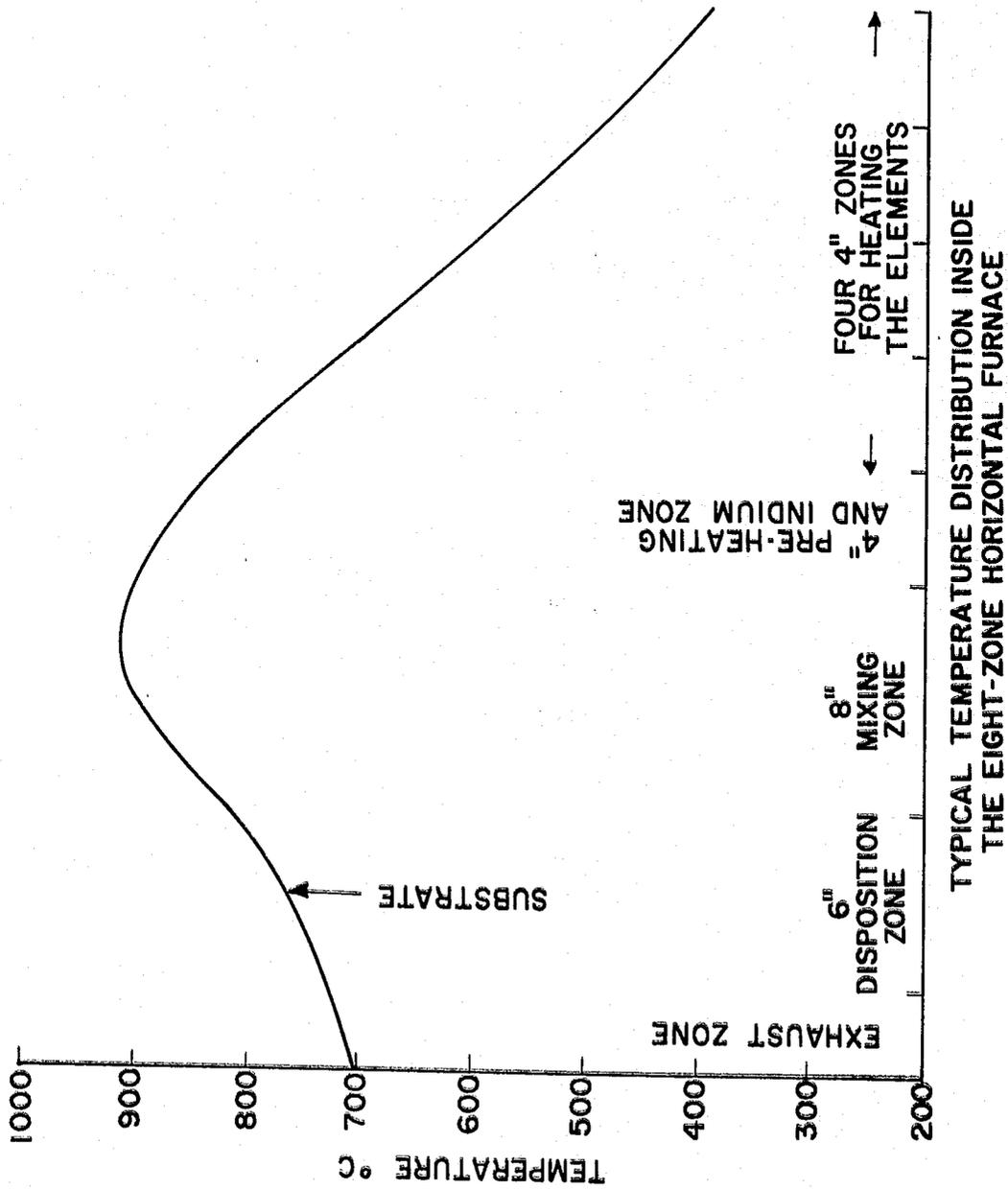


FIG. 4

VAPOR PHASE GROWTH OF GROUPS III-V COMPOUNDS BY HYDROGEN CHLORIDE TRANSPORT OF THE ELEMENTS

ORIGIN OF THE INVENTION

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72 Stat. 435; 42 USC 2457).

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a method for the vapor phase production of binary, ternary, and quaternary compounds derived from the elements of Groups III-V by hydrogen chloride transport of the respective elements.

2. Description of the Prior Art

The compounds derived from the elements of Groups III-V are useful as semi-conductors, and the alloys exhibit a wide range of useful electrical and optical properties, thereby making them extremely useful for a wide variety of electronic applications. Among these include electro-optic and microwave devices, high-temperature applications, and electron emitting phenomenon. Unfortunately, the preparation of these materials is rather difficult. Many of the difficulties can be avoided, however, when vapor phase crystal growth methods are employed, particularly because of the low growth temperatures that are possible by these methods. Further, vapor phase growth facilitates the preparation of these compounds in a thin-layer epitaxial arrangement, which is often essential for optimum use in various electronic structures.

Typical compounds of Groups III-V elements from which epitaxial films are prepared include the well-known binary compounds gallium arsenide, indium arsenide, and the corresponding gallium and indium phosphides. Typical ternary compounds can be represented by the group $GaAs_xP_{1-x}$, wherein x is greater than 0 and less than one.

Many of the present methods for epitaxially growing such compounds have serious disadvantages. Some of the prior art methods make use of the gaseous hydrides such as AsH_3 , PH_3 , and SbH_3 . Unfortunately, these latter gases are extremely expensive and are difficult to obtain in a highly pure form. They also tend to dissociate during storage.

The use of the chlorides of the Groups III-V elements also presents serious difficulties, it being generally difficult to control their transport because of the sharp dependency of their vapor pressure on the temperature. The growth reactions for the Group III-V compounds are actually incomplete chemical reactions, involving the sub-chlorides of the elements, rather than the higher chlorides.

Gallium arsenide has been prepared by transporting elemental gallium by HCl gas and the elemental arsenic by hydrogen. There has also been described a process for the production of large single crystals of the Group III-V compounds wherein the corresponding crude polycrystalline form is reacted with a hydrogen halide to form a complex mixture, the vapor of which is then cooled so that the original compound is reconstituted or reformed, being deposited in a very pure single crystalline form.

In the present invention it has now been found possible to prepare the Group III-V compounds solely by HCl transport of the Group III-V elements. The present method is significantly simpler and much more economical than those of the prior art and permit the epitaxial growth of a wide variety of binary, ternary, and quaternary Group III-V compounds.

SUMMARY OF THE INVENTION

The present invention provides a vapor phase method of forming binary, ternary, and quaternary compounds from the elements of Groups III-V by hydrogen chloride transport of the constituent elements. The process comprises the steps of:

a. passing a carrier gas consisting of hydrogen and hydrogen chloride, containing 1% to 10% of hydrogen chloride by volume separately over two to four elements of Groups III-V kept at temperature below their sublimation temperature or boiling point, but at a temperature sufficient for their reaction with the hydrogen chloride, whereby the elements combine with the hydrogen chloride to form the corresponding subchlorides; and

b. transporting the sub-chlorides obtained in (a) to a deposition zone containing a single crystal substrate, whereby the elements deposit on the substrate, with the rate of flow of carrier gas over each of the elements being adjusted so that the elements are deposited on the substrate in sufficient amounts to provide a binary, ternary, or quaternary compound consisting of elements of Groups III-V.

The preferred elements of Groups III-V are gallium, indium, arsenic, and phosphorous.

The method of the present invention is particularly effective for the manufacture of gallium arsenide crystals.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1. is a side elevational view of the growth tube used in the invention.

FIG. 2 is a top plan view of the growth tube; and

FIG. 3 is a cross-sectional front view of the growth tube;

FIG. 4 represents a typical temperature distribution in the growth tube when placed in an 8-zone horizontal furnace using independently controlled resistance heating units of lengths varying from 4inch to 8inch each.

DETAILED DESCRIPTION OF THE INVENTION

The growth apparatus comprises an 8-zone horizontal external furnace containing independently controlled resistance heating units of lengths varying from 4inch to 8inch each. Growth tube 13 is placed inside of this external furnace. The elements are placed in graphite boats, which are then inserted into the separate source tubes 1-4. Each graphite boat is positioned within the source tube so that the element it contains is heated to the necessary temperature. Examples of some typical temperatures involved are listed below:

ELEMENT	TEMPERATURES
Gallium	650°-850°C
Indium	750°-950°C
Arsenic	400°-550°C
Phosphorous	300°-500°C

The growth tube 13, shown in FIGS. 1-3, is made of fused quartz. There is a separate source tube for each element. It is preferred to coat the inside of the growth tube with carbon, by pyrolytic cracking of pure acetone, in order to prevent the impurities in the silica of the tube from diffusing into the crystal being grown and also to shield the silica tube from reaction with highly abrasive compounds, such as the chlorides of aluminum.

Referring to the Figs., the substrate 8, which is a single crystal is polished and etched and mounted on a fused quartz substrate holder 7.

In the preparation of gallium arsenide and gallium phosphide crystals it is found advantageous to use single crystals as the substrate that are oriented in the $\langle 100 \rangle$ direction and to polish and etch them in Caro's acid or a 1% bromine in methanol solution.

The separate elements of Group III-V are placed in graphite boats in tubes 1-4. As mentioned above, since the entire tube is placed in an 8-zone horizontal furnace (not shown) using independently controlled resistance heating units, each graphite boat is positioned in the tube at a location having the proper temperature environment.

A fine tube 5 is provided for purging and cleaning the system after crystal growth by passing hydrogen chloride gas through it while simultaneously passing hydrogen through tubes 1-4. During the growth phase, however, only hydrogen gas is passed through tube 5, generally at a rate of about 100 cc/min. Any dopants in gaseous form, such as H_2Se or NH_3 , can also be passed through tube 5. The versatility of the system can be increased by transporting the dopants through an optional side tube 6. If such a tube is used, a vertical heater is added to the furnace in order to provide proper temperature control for the interior of this tube. An exhaust tube 9 is provided to vent the exhaust gases. Rod 10 permits the positioning of the substrate 8 in the growth tube. An exhaust zone heater assists in etching out the deposition from inside the tube during the cleaning process and is also used for preheating the substrate before it is inserted into the growth or deposition zone 12. The exhaust gases are bubbled through an inert low vapor pressure oil.

All five longitudinal tubes 1-5 lead into the reaction zone 11, which in turn leads into the deposition or growth region 12.

After positioning and heating the substrate 8 within the proper region 12 of the growth tube, the system is thoroughly purged with hydrogen at the equilibrium temperature distribution, and the desired elements of Groups III-V are each separately placed in graphite boats and positioned in tubes 1-4, each element-containing graphite boat being positioned within each tube such that the horizontal furnace heats each element to the required temperature. The carrier gas, consisting of hydrogen and hydrogen chloride, is then passed through each of tubes 1-4 such that the elements in the graphite boats react with the hydrogen chloride. It is important to ensure that enough surface area of the elements is exposed to the carrier gas so that no unreacted hydrogen chloride reaches the reaction chamber 11 and deposition zone 12.

Thus, the present method utilizes all of the Group III-V elements in their elemental form, which are readily available in high purity. Upon contact with the carrier gas comprising HCl and hydrogen, they are con-

verted into the sub-chlorides upon reaction with the HCl. The sub-chlorides are easily transported in the vapor phase by the hydrogen. The elements of Groups III-V are kept at temperatures below their boiling or sublimation temperatures, but at a high enough temperature so that they rapidly react with the hydrogen chloride in the carrier gas.

FIG. 4 shows a typical temperature range distribution within the 8-zone horizontal furnace into which is placed the growth tube 13.

As mentioned above, enough of the surface area of the elements must be exposed to the carrier gas to ensure that no unreacted hydrogen chloride reaches the deposition zone 12. The rate of transportation of the elements is accurately controlled by adjusting the rate of flow or dilution of the carrier gas flowing over them. As especially preferred range of concentration of hydrogen chloride in the carrier gas is 1%-10% of hydrogen chloride by volume. The volume of carrier gas flowing over each element in each source tube is usually kept below about 300 cc/min.

In a typical example, such as the preparation of a gallium arsenide type compound, the growth tube is purged with hydrogen, at the equilibrium temperature distribution, after two graphite boats, one containing gallium and the other arsenic, are appropriately positioned in any two of tubes 1-4. Growth is then started by passing the carrier gas over gallium and arsenic. After several minutes, a gallium arsenide crystal substrate, oriented in the $\langle 100 \rangle$ direction, is placed on the quartz substrate holder 7 and introduced into the deposition region 12 of the growth tube and growth is continued for about 10 minutes. Thereafter, about 20 cc/min. of the carrier gas is diverted every five minutes from the gallium tube (if needed) to a tube containing another Group III element, until the desired composition is achieved. The substitution of gallium by the corresponding Group III element is normally not in the ratio of the respective flow rates of the hydrogen chloride-containing gas over them, and therefore the system must first be calibrated to determine the flow rates required to obtain different compositions.

Substitution for arsenic (if needed) by a Group V element is carried out in a similar way.

Alternatively, the system can be first purged with hydrogen at the equilibrium temperature distribution, and the carrier gas passed over the arsenic for 5-10 minutes. At this time the substrate can then be introduced into the deposition growth region 12, and the flow continued for about 10 minutes. Crystal growth can then be started by simultaneously passing the carrier gas over gallium. Substitution of other elements for the gallium or arsenic is accomplished by flowing the carrier gas over the desired elements. By changing the carrier gas flow rates over the various elements, the crystal composition can be graded and controlled to almost any desired product. As mentioned above, since the ratio of the elements in the grown crystal are not the same as the ratio of the flow rates over the respective elements, the system must be first calibrated to determine composition as a function of the various flow rates. This can be done by simple routine experimentation.

Junctions can be grown by switching on the carrier gas flow over the dopants, if used in the system. Typical dopants include zinc, magnesium, and the like, which impart the desired electrical resistivity properties into

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the compound. As pointed out previously, these dopants can be separately introduced into the growth tube by means of optional tube 6.

It will be appreciated that the exact temperature ranges employed will be determined by the specific Group III-V elements selected. It is only necessary to heat each element to a high enough temperature so that it reacts with hydrogen chloride in the carrier gas. With regard to the temperature in the deposition zone, it should be at a temperature sufficient to permit the deposition of a single crystal form of the compound from the reaction mixture.

By means of the present method gallium arsenide crystals have readily been prepared having good single-crystal qualities of the epitaxial layer.

What is claimed is:

1. A method of forming binary, ternary, and quaternary compounds derived from elements of Group III and Group V, which consists essentially of the steps of:

- a. passing a carrier gas consisting of hydrogen and hydrogen chloride, containing 1% to 10% of hydrogen chloride by volume separately over two to four elements of Group III and Group V, at least one of said elements being a Group III element and one being a Group V element, said elements being in separate source tubes and kept at a temperature below their sublimation temperature or boiling points, but at a temperature sufficient for their reaction with the hydrogen chloride, whereby the elements combine with the hydrogen chloride to form the corresponding sub-chlorides such that es-

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sentially no unreacted hydrogen chloride remains; and

- b. transporting the sub-chlorides obtained in (a) to a deposition zone containing a single crystal substrate derived from at least one Group III element and one Group V element whereby the elements deposit on the substrate, with the rate of flow of carrier gas over each of the elements being adjusted so that the elements are deposited on the substrate in sufficient amounts to provide a binary, ternary, or quaternary compound consisting of elements of Group III and Group V.

2. The method of claim 1 wherein the elements of Group III and Group V are selected from the group consisting of gallium, indium, arsenic, and phosphorous.

3. The method of claim 1 wherein the substrate is a gallium arsenide crystal oriented in the <100> direction and the carrier gas is passed separately over gallium and arsenic.

4. The method of claim 3 wherein the gallium is heated at a temperature between 650°C to 850°C and the arsenic is heated at a temperature between 400°C to 550°C.

5. The method of claim 1 wherein the volume of carrier gas flowing over each element in each source tube is below about 300 cc/min.

6. The method of claim 4 wherein the volume of carrier gas flowing over the gallium and arsenic in each source tube is below about 300 cc/min.

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