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[50] Field of Search..... 117/201,
 106 A; 23/209; 252/62.3; 148/174, 175

[56] **References Cited**

UNITED STATES PATENTS

3,178,313	4/1965	Moest.....	117/201
3,210,149	10/1965	Eland.....	252/62.3 X
3,420,704	1/1969	Ramey.....	117/106 X
3,462,323	8/1969	Groves.....	148/175
3,472,685	10/1969	Marfaing et al.....	117/201

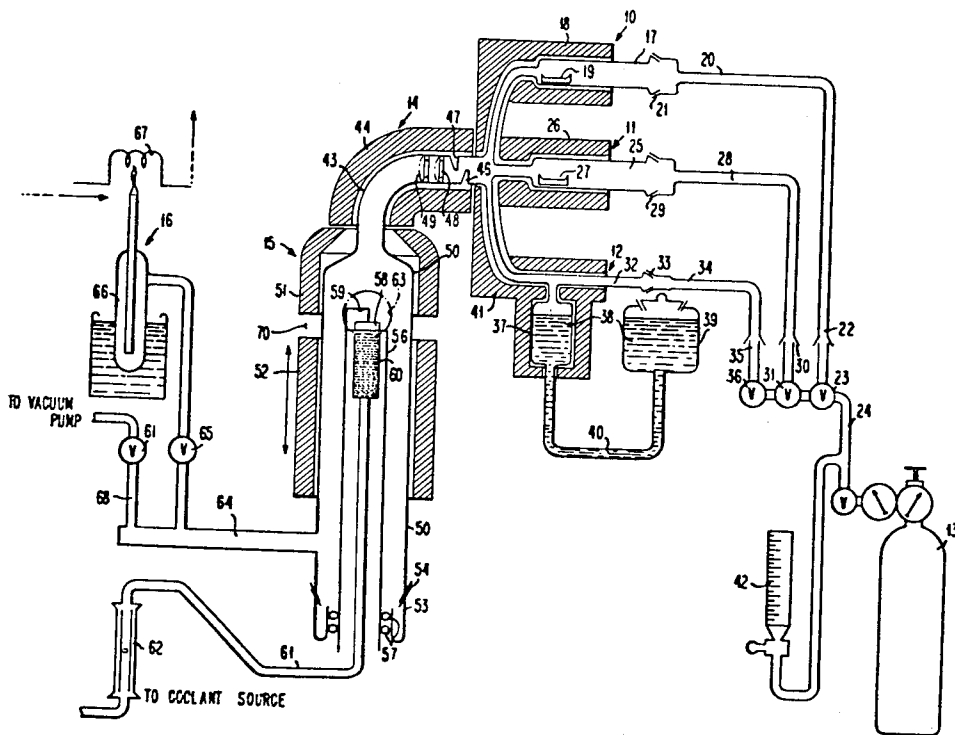
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[54] **METHOD FOR VAPOR GROWING TERNARY COMPOUNDS**
 7 Claims, 4 Drawing Figs.

[52] U.S. Cl..... **117/201,**
 117/106 A, 252/62.3 R

[51] Int. Cl..... **H011 7/36,**
 C23c 13/04

ABSTRACT: Ternary epitaxial films are grown from a gaseous mixture consisting of mercury, cadmium, and tellurium mixed with an inert or unreactive gas such as hydrogen. The mixture is heated to a temperature to prevent binary combinations and then rapidly cooled to the point of supersaturation by flowing the mixture through a thermal gradient having equithermal lines substantially parallel to the growth surface of a substrate.



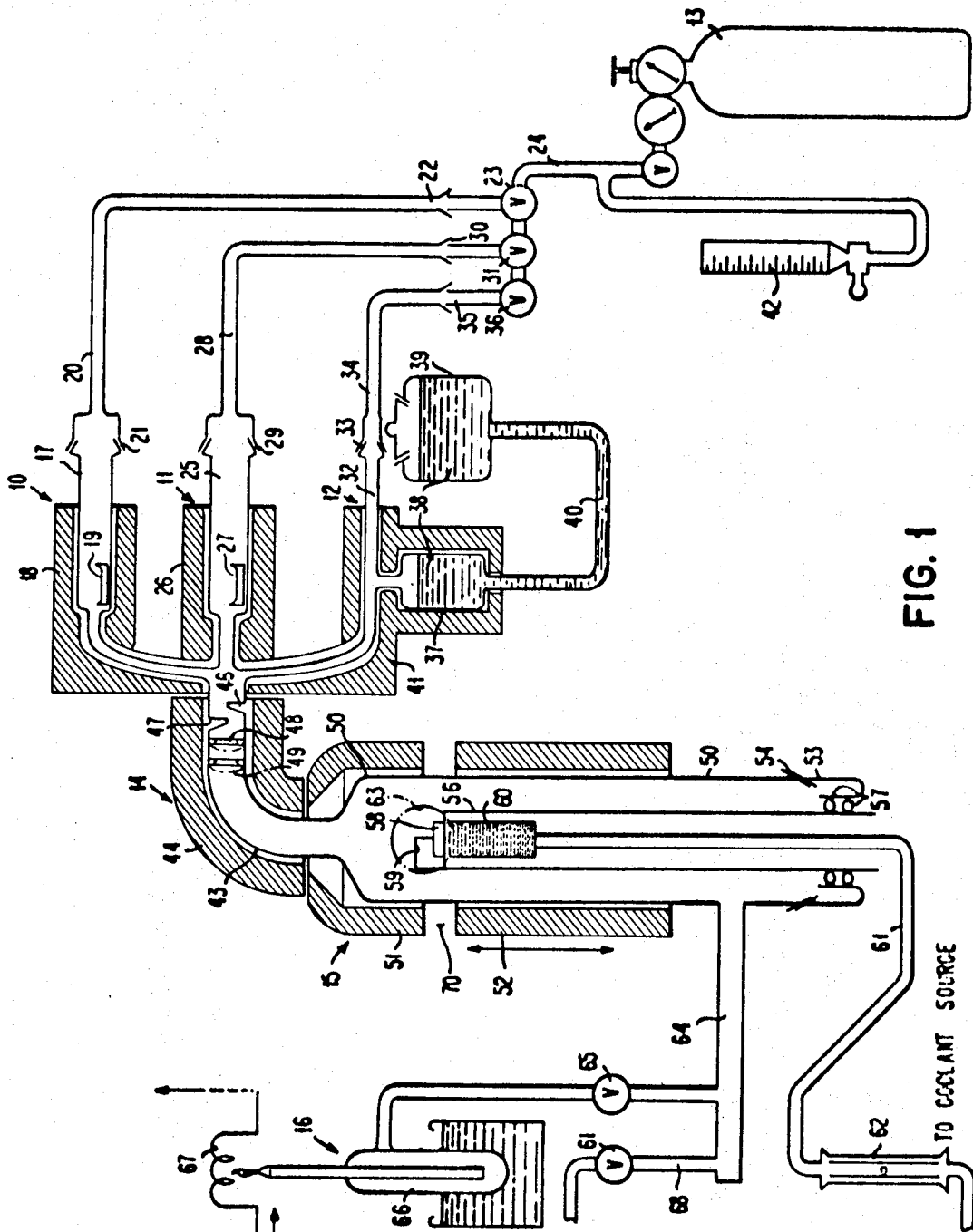
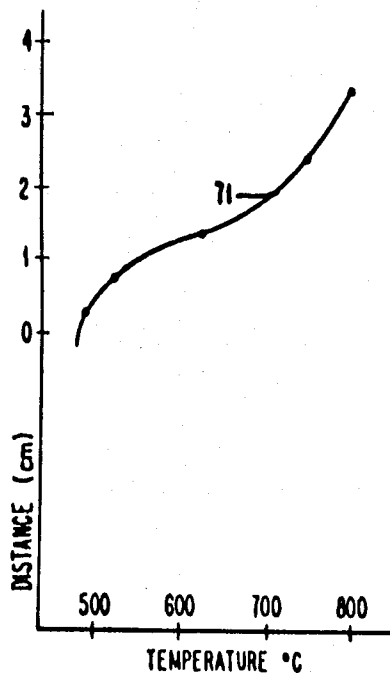
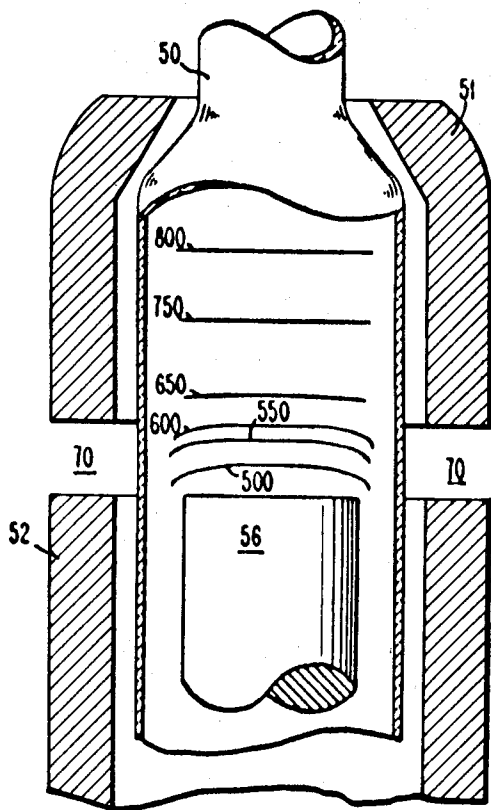
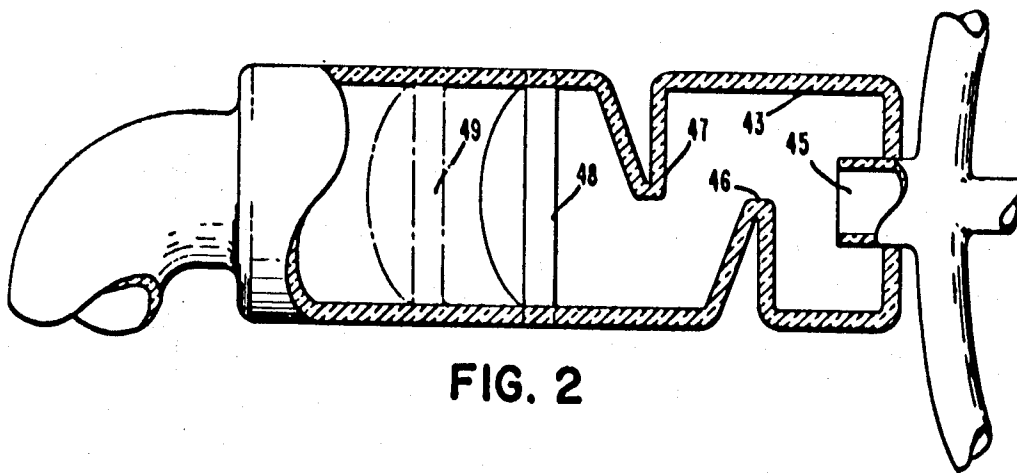


FIG. 1

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METHOD FOR VAPOR GROWING TERNARY COMPOUNDS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to semiconductor devices in the form of ternary compounds and particularly to a method and apparatus for vapor growing epitaxial films using elements and compounds from the II-VI valence groups.

2. Description of the Prior Art

In the prior art of vapor growing epitaxial films, it was considered essential to use disproportionation or other chemical reactants such as the halogens and their compounds. These were considered to act as transport agents to the elemental reactants from which the semiconductor films are made. Unfortunately, for many applications, the resultant films contained a proportion of the halogen element and thereby disturbed their molecular composition.

In a copending application of Carpenter, McDermott, Manley, Riley, Ser. No. 763,307, filed on Sept. 27, 1968, and assigned to the assignee of the present invention, it was shown that epitaxial films can be grown from the vapor phase without the presence of a disproportionation reactant, and that stoichiometric films can be achieved by condensation of the film constituents directly from the vapor phase to the solid state. In that application, the system used one of the constituent reactants (e.g., Hg) as the transport agent and the apparatus was designed as a closed system. Such a system, while useful for producing high grade ternary epitaxial films would have some limitation for larger scale production requirements. Using the mercury reactant in a large scale system would require excessively elaborate apparatus to maintain the essential temperature and pressure conditions necessary to avoid side reactions detrimental to the growth process. Overpressure control of mercury to effect the ternary combination in the closed system, and furthermore, uniform crystal film composition over a large deposition area, were difficult to achieve.

SUMMARY OF THE INVENTION

The broad object of this invention is to provide a method and apparatus capable of vapor growing ternary epitaxial films at larger production rates.

It is a specific object of this invention to provide a method and apparatus for vapor growing ternary epitaxial films consisting of II-VI elements having uniform composition over a larger deposition area to produce larger epitaxial film crystals.

It is a further specific object of this invention to provide a method and apparatus for vapor growing epitaxial films of mercury cadmium, and tellurium which are useful as infrared detector devices and particularly infrared mosaic detectors.

It is also an object of this invention to provide a method and apparatus for vapor growing epitaxial films of mercury, cadmium, and tellurium at relatively low pressures and temperatures without using disproportionation reactant agents for growth and carrier control.

The above, as well as other objects, are attained in accordance with the practice of this invention by forming a gaseous mixture consisting of growth reactant gases from elements of the II-VI valence groups and an inert transport gas such as hydrogen, argon, and mixtures thereof. In the preferred form, the constituent gases are added separately to individual streams of the carrier gas, after which the individual streams are combined and mixed to form a uniform distribution of the ternary elements and the carrier gas. During the combining step, heat is applied to set a temperature level high enough to prevent binary reactions to occur. The mixture is then rapidly cooled to simultaneously supersaturate each of the growth constituents forcing them to condense simultaneously on the growth surface of a seed crystal substrate. It is a feature of this invention that the rapid cooling is effected by passing the ternary gas and carrier mixture through a thermal gradient having equithermal lines substantially parallel with the growth surface of the substrate.

The apparatus for practicing the present invention is of the "open" tube type, that is, the maximum pressure within the apparatus does not exceed a pressure much above atmospheric. In the preferred embodiment, the apparatus comprises plural source furnaces connected in parallel to a common carrier gas source. Source materials volatilized to the appropriate temperature and pressures are added to the gas streams of the carrier gas in the source furnaces. A mixing furnace having a common input from the source furnaces provides a uniform distribution of the reactant gases and the carrier gas for feeding to a reaction furnace. The mixing furnace comprises heating means operable simultaneously with the mixing action to maintain the temperature of the mixture at a level which inhibits binary reactions within the mixing chamber.

A growth substrate is mounted on a pedestal adjustably movable within the reaction chamber. A cooling means supplies air coolant to the substrate. Heating coils, one of which is movable, surrounds the reaction chamber to produce high temperatures necessary to maintain the ternary mixture in its vapor phase until it is very close to the substrate growth surface. A flat equithermal profile is achieved by separating the coils to provide a heating gap along the reaction chamber in the region of the deposition substrate. Unreacted gases pass from the reaction chamber, are condensed and the carrier gas passed into the atmosphere. With such an apparatus, continuous high rate film growing may be practiced, pressures within the apparatus are low thereby assuring greater safety, and relatively large epitaxial films with uniform composition are obtained. An additional advantage of this system resides in the fact that the source materials may be elemental in nature and when processed through the system are essentially being distilled. This insures freedom from contaminants such as copper which may be present in source materials even of the highest purity.

The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of preferred embodiments of the invention, as illustrated in the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional schematic of a vapor growing apparatus for practicing the present invention;

FIG. 2 is a sectional view of a mixing chamber used in the apparatus of FIG. 1;

FIG. 3 is a sectional detail of the reaction chamber of the apparatus of FIG. 1 illustrating a thermal map for the reaction chamber for a particular setting of heating coils for the reaction chamber; and

FIG. 4 is a graph of a thermal profile of the thermal gradient of FIG. 3 taken along a center line 4-4 shown in FIG. 3.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to FIG. 1, the improved vapor growing apparatus comprises source furnaces 10, 11, and 12 connected in parallel between a source 13 of an inert carrier gas and a mixing furnace 14, which in turn is connected to a reaction furnace 15 connected to apparatus 16 for venting the inert gas to the atmosphere. Source furnace 10 comprises a quartz chamber 17 wound with a heating coil 18. A supply of elemental cadmium 19, preferably in the form of pellets in a quartz boat, as shown in the above-mentioned copending application, is located within the heating zone established by coil 18. A current supply and regulating means of suitable type (not shown) which is independently operable, is connected to heating coil 18 to maintain temperature levels to effect volatilizing of the elemental cadmium into the hydrogen gas stream as it flows through chamber 17. The channel for supplying hydrogen gas to chamber 17 comprises tube 20 connected to chamber 17 via airtight seal 21, and through flow meter 22 and flow valve 23 to a common flow line 24.

Source furnace 11 comprises a quartz chamber 25 wound with heating coil 26 electrically connected and controlled in

essentially the same manner as coil 18 of furnace 10. A supply 27 of elemental tellurium, preferably in pellet form in a quartz boat, or the like, is located within the heating zone of coil 26 to be volatilized and added to a hydrogen gas stream flowing through chamber 25. The carrier gas channel to furnace 11 comprises a tube 28 connected by an airtight seal 29 to chamber 25 and through flow meter 30 and flow valve 31 to supply line 24. Source furnace 12 comprises a T-shaped quartz tube 32 having one branch connected by an airtight seal 33 to tube 34 and through flow meter 35 and valve 36 to supply line 24. The second branch of chamber 32 is connected to a mercury supply well 37. Liquid mercury 38 is fed by gravity from an external reservoir 39 through connecting tube 40 to well 37. An electrical coil 41 which is wound entirely around the well 37 as well as the entire junction area of tube 32 is electrically connected to current source and regulating means of a suitable type for vaporizing the mercury at predetermined temperature and pressure levels for addition to a hydrogen gas stream flowing through tube 32. The connection of tube 32 to well 37 is preferably made long and the winding of coil 41 is such as to allow a measure of preheating of the mercury vapors prior to their addition to the hydrogen gas stream in tube 32. The flow of hydrogen gas from source 13 is suitably measured for regulation means such as bubble column 42, or the like, connected to supply line 24.

In its preferred form, the mixing furnace 14 comprises a cylindrical quartz chamber 43 entirely wound with a heating coil 44 which is electrically connected to suitable current source and regulating means (not shown) which may be independently operable to maintain temperature of the mixing chamber 43 at levels to assure proper constituent control. As best seen in FIG. 2, the mixing chamber 41 has a single tube input 45 connected in common with the outputs of chamber 17, 25 and tube 32 of source furnaces 10, 11, and 12, respectively. To effect thorough mixing and uniform distribution of the constituent elements in the hydrogen carrier gas stream, mixing chamber 43 is provided with a series of baffles 46-49 arranged to produce eddying within the hydrogen stream as it leaves tube 45. While various types of baffling can be provided and while the number of baffle elements may vary, the baffles 46-49, as seen in FIG. 2, are four in number and are preferably integral protrusions formed from the walls of chamber 43. Such baffles are formed by heating to soften the quartz walls. Then, using wedge shaped tools, having straight leading edges, the walls are impressed inwardly with the straight and sloping surfaces as shown, with the innermost edges penetrating the chamber to a point in line with the center line of input tube 45. As seen in FIG. 2, the baffles 46 and 47 are opposed at spaced longitudinal positions. Baffles 48 and 49 are similarly constructed and shaped except that they are oriented 90° from the positions of baffles 46 and 47. The longitudinal spacing of the baffles is a function of rate of gas flow, but is in the preferred case set to produce eddying in 3 dimensions thereby assuring complete and thorough mixing to effect uniform distribution of the constituent gases throughout the carrier gas stream. When forming the baffles 46-49 in the manner described, care must be exercised to assure that the upper edge of the baffles are substantially diametrical, including the parts adjacent the walls of chamber 43. Otherwise, some flow will occur around the baffles unimpeded and produce inadequate mixing.

The reaction furnace 15 comprises a cylindrical quartz reaction chamber 50, a pair of coaxial heating coils 51 and 52 wound thereon, and a means for supporting a growth substrate 55 at a selectable growth site position within the chamber relative to the heating coils. The reaction chamber 50 is preferably designed with a removable cylindrical section 53 which is provided with a central opening and joins with the rest of the reaction chamber at airtight seal 54. The substrate support comprises a cylindrical pedestal tube 56 which is inserted through the central opening of bottom section 53. Sealing means, such as O-rings 57, are provided between pedestal tube 56 and chamber section 53. A growth substrate 58 is at-

tached by suitable means such as spring clip 59. Cooling means comprises a silver heat sink cylinder 60 inserted within pedestal tube 56, and tube 61, connected through flow meter 62 to an air coolant source. Both the heat sink 60 and spring clip 59 structures may be other than the type shown in the above-mentioned depending application. A viewing port 63 is provided in reaction chamber 50 in the general area of the desired growth site. Venting of the carrier gas from the system is provided by tube 64 connected through valve 65 to a cold trap 66. If the carrier gas is to be burned when vented, as in the case where hydrogen gas is used, an ignition device, such as coil 67, may be used. The system is also connected to a vacuum pump from tube 64 through tube 68 and valve 69.

In the preferred embodiment of this invention, the heating coils 51 and 52 are connected to separate current source and regulator means. This permits flexibility in controlling the heating effects necessary to control the thermal gradients essential for vapor growing ternary compounds. In addition, heating coil 52 is wound in such a manner that it is movable longitudinally along reaction chamber 50. By the movement of coil 52, a separation 70 is provided which produces a thermal gap in the heating field of the coils 51 and 52. By varying this gap, the thermal gradient profile, and thus the composition control of film grown on substrate 58 is obtained.

In order to operate the apparatus of FIG. 1 to vapor grow epitaxial films, certain preliminary procedures are necessary. Substrate 58 is selected to have the desired crystal structure then polished and cleaned. A suitable crystal would be a monocrystal of Cd Te of a nominal thickness of 10 mils cut from an ingot along the [100] crystallographic plane. Cleaning and polishing may be performed as described in the above-mentioned depending application. The selected crystal 58 is then attached to the end of pedestal 56 by spring clip 59 and inserted within reaction chamber 50 through the opening in bottom section 53 (which has been assembled and sealed at 54) using O-rings 57 to effect reaction chamber sealing. Similarly, source materials 19 and 27 of cadmium and tellurium, respectively, are placed in heating zone position within source furnaces 10 and 11 and liquid mercury 38 adjusted to the desired level within furnace 12 after which the reservoir 39 is blocked to close the mercury feed system.

Following these procedures, and with all external joints firmly sealed, the system is evacuated to an initial pumpdown level through valve 69 to eliminate oxidizing gases and impurities. Hydrogen gas which flows from source 13 is then turned on and vented through the apparatus to atmosphere where it is ignited by coil 67. At the same time, the vacuum pump is stopped and valve 69 closed. A back-etch operation of substrate 58 may then be performed according to well-known techniques to further polish the growth surface of substrate 58. This may be done in the apparatus of FIG. 1 by turning on the reaction furnace 15, mixing furnace 14, and the cadmium and mercury source furnaces 10 and 12. Source furnace 11 is not turned on. For the back-etch operation, coil 52 is moved virtually adjacent the coil 51, thereby eliminating gap 70, and both are energized to a common temperature level. For example, with a substrate of Cd Te, furnace 12 has a temperature of 300° C. and mixing furnace 14, and source furnaces 10 and 12 have temperature settings of 850° C., 370° C., and 315° C., respectively. Heating takes place for a period of 15-20 minutes, or until the substrate surface 58 is observed through aperture 63 to take on a glossy appearance.

Following the back-etch operation, coil 52 of reaction furnace 15 is moved along chamber 50 to the desired separation of gap 70 and coils 51 and 52 energized to the desired operating temperature levels for vapor growing. At this point in the operation streams of hydrogen gas enriched with cadmium gas and mercury vapor, flow through the system, are mixed in furnaces 14 and passed through to the reaction chamber 50. Since a growth reaction does not yet take place, mercury and cadmium will condense in the lower portion of chamber 50 and collect in bottom section 53. Lastly, the source furnace 11 is now turned on to volatilize tellurium from source 27 into the

hydrogen gas stream flowing in chamber 25. At the same time, cooling air is supplied to heat sink 60 to drop the temperature of substrate 58 to the desired film growing level. With all sections of the system thus operating, a crystalline ternary epitaxial film becomes deposited on the upper surface of the substrate 58. After a predetermined operating time to obtain the desired film growth, the source furnaces 10 and 11, and the mixing and reaction furnaces 14 and 15 are turned off. The source furnace 12, however, is allowed to remain on after all the other parts of the system are turned off to allow the mercury vapor pressure to remain within prescribed levels in reaction chamber 50 to prevent mercury from being volatilized from the grown film after air to heat sink 60 is cut off. Furnace 12 continues to operate until the reaction chamber 50 reaches a temperature of approximately 100° C. for Hg Cd Te films, then it is shut off and the system opened to the atmosphere.

Using the above operating procedures, epitaxial films of Hg Cd Te were grown using hydrogen as the carrier gas with a flow rate of 60 cc./minute, reaction chamber coil gap setting of 1 cm. and the following temperature settings:

Source Furnace 10	(cadmium)	305° C.
Source Furnace 11	(tellurium)	430° C.
Source Furnace 12	(mercury)	310° C.
Mixing Furnace 14		850° C.
Reaction Furnace 15	(coil 51)	800° C.
Reaction Furnace 15	(coil 52)	530° C.
Substrate		480° C.

It should be noted that a minimum substrate temperature must be maintained to promote epitaxy or single crystal growth and prevent dendrite growth which can be a problem at substrate temperatures much below 450° C. and the source temperatures mentioned above. In the preferred form of practicing this invention, stoichiometry is controlled in the growing layer by fixing the cadmium source temperature and, thus, its overpressure and then varying the amount of tellurium in the gas stream. When the amount of tellurium is the same as cadmium due to the relatively low substrate temperature, just Cd Te would be formed and there is very little Te available for reaction with Hg. By adding Te in excess of the cadmium present, some free Te is available to react and incorporate Hg in the growing crystal lattice. With the substrate temperature sufficiently low, the supersaturation of Te and Hg in the gas phase is sufficient to cause a complete reaction on the substrate. Under the conditions described, a rise of substrate temperature of 20-50° C., while not appreciably affecting the Te-Cd reaction, is capable of affecting the quantity of Hg chemically reacting in the growing crystal. Thus, chemical composition is controlled by adjusting the ratio of constituents in the gas phase and by controlling the substrate temperature.

In accordance with this invention, the growth of ternary Hg Cd Te epitaxial films requires cooling the substrate 58 at the minimum temperature and yet locating it as close to the mixing temperature (800° C.) to thereby produce a very sharp temperature gradient as close to the substrate as possible. This prevents depletion of Cd and Te by spontaneous nucleation prior to arrival at the substrate. An example of a thermal profile for a gap setting of 1 cm. with temperatures of coils 51 and 52 set at 800° C. and 530° C. respectively, and a substrate temperature of 480° C. and a flow rate of 30 cc./min. is shown in FIGS. 3 and 4. Curve 71 illustrates the thermal profile taken along the center line through reaction chamber 50 through heating zone of coil 51 to the growth surface of substrate 58. As there illustrated, the temperature of the gas mixture changes from over 600° C. to below 500° C. within a space of approximately 1 cm. to a point of about 0.5 cm. from the substrate surface. In passing through this sharp a gradient, vapors of cadmium, tellurium, and mercury become supersaturated and, since they are very proximate the growth surface of substrate 58, condensation occurs thereon.

As further illustrated in FIG. 3, the equithermal lines above the growth surface of substrate 58 are substantially parallel with the growth surface which is preferably flat and the tem-

perature across the growth surface is uniform over substantially the entire surface. Since film growth is a function of substrate temperature, uniformity of substrate temperature assures uniformity of composition over the growth surface. This type of thermal profile is achievable by adjusting the separation 70 between coils 51 and 52 to effectively produce a gap in the thermal field in the region of the substrate 58. By contrast, with a single coil wound on the reaction chamber, the thermal profile would have equithermal lines of curvilinear shape of substantially larger radius extending from end to end of the substrate surface. Thus, a temperature gradient exists across the growth surface. Thus, composition would vary in the film grown on the substrate surface. Detector crystals cut from such film would be of variable semiconductive properties and their use in a multiple detector configuration presents substantial performance and circuit design problems. By using the separation gap to flatten the thermal profile lines, films of up to ½ square inches have been grown from which a plurality of crystals may be cut having substantially the same semiconduc-

tor properties. Examples of other actual growth conditions which produced high quality epitaxial films are shown in the following table.

TABLE I

Growth Run No.	Analysis in % X-ray Fluorescence Counts			Heat Sink Temperature °C.	
	Hg	Cd	Te		
23 MK III	22.5	30.1	47.4	520	
24 MK III	27.6	27.9	44.5	515	
25 MK III	41.8	19.9	38.3	510	
26 MK III	60.3	7.1	32.6	505	
Furnace Source Temperature °C.				Reaction Furnace Coil Separation	
Hg Cd Te					
23 MK III	315	370	510	1 cm.	
24 MK III	315	370	510	1 cm.	
25 MK III	315	370	510	1 cm.	
26 MK III	315	370	510	1 cm.	
Mixing Furnace Temperature °C.				Reaction Furnace Coil 51 Coil 52	
23 MK III	850			800	530
24 MK III	850			800	530
25 MK III	850			800	530
26 MK III	850			800	530

In all the above samples, the substrate was a Cd Te monocrystal of a nominal thickness of 10 mils cut along the [100] crystallographic plane, the carrier gas was hydrogen, and the source materials were 99.9999 percent purity cadmium and tellurium. The growth times were 2 hours in all cases with a 60 cc./min. flow rate through each of the source furnaces 10, 11, and 12. The films produced having substantially uniform composition were produced in sizes from ¼ to ½ square inches. By making the growth apparatus longer, larger size crystals are obtainable.

While the above examples show use of Cd Te growth substrates, other materials, such as Pb Te and Sn Te may be used. Also, while hydrogen gas was used in all specific examples, argon and argon hydrogen mixtures may serve as the carrier gas.

While the invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that the foregoing and other changes in form and details may be made therein without departing from the spirit and scope of the invention.

We claim:

1. A method for vapor growing ternary epitaxial films on a substrate comprising the steps of:

forming a gaseous mixture consisting of growth reactant gases from elements of II-VI groups and an inert transport agent;
 heating said gaseous mixture to a temperature which prevents binary combinations of said reactant elements;
 forming a sharp thermal gradient proximate the growth surface of said substrate by
 cooling said substrate to a temperature at which condensation of said reactant gases from said mixture occurs, and by
 heating the regions surrounding said substrate in a manner which produces a thermal gradient immediately above the growth surface; and
 flowing said mixture through said gradient into contact with said substrate to rapidly supersaturate the growth reactant elements within said mixture to effect film growth of a ternary compound thereon.

2. A method for vapor growing ternary epitaxial films in accordance with claim 1 in which said gaseous mixture is formed by adding each growth reactant gas to separate streams of said transport agent, followed by combining said streams into a

common stream and flowing said stream through a mixing device to produce uniform distribution of said reactants in said transport agent.

3. A method for vapor growing ternary epitaxial films in accordance with claim 2 in which said heating to prevent binary combinations of said reactant gases is done concurrently with said mixing of said separate gas streams.

4. A method for vapor growing ternary epitaxial films in accordance with claim 1 in which said reactant gases consist of elemental mercury, cadmium, and tellurium and said transport agent is selected from a group consisting of hydrogen argon, or a mixture thereof.

5. A method for vapor growing ternary epitaxial films in accordance with claim 1 in which the cooling of said substrate and the heating of the region surrounding said substrate is done in a manner which produces a thermal gradient immediately above the growth surface of said substrate having equithermal lines substantially parallel with said growth surface.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,619,282 Dated November 9, 1971

Inventor(s) Gerald W. Manley, Philip S. McDermott,
~~Edward S. Pan and Ralph J. Riley~~

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

On the cover sheet, following the official title [54], change "7 claims, 4 Drawing Figs." to read --5 claims, 4 Drawing Figs.--.

Column 1, after the title (lines 1 and 2) and before "Background of the Invention" (line 4) insert the paragraph --The invention herein described was made in the course of, or under a contract with the Department of the Navy.--.

Signed and sealed this 9th day of May 1972.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents