

United States Patent

[11] 3,619,283

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

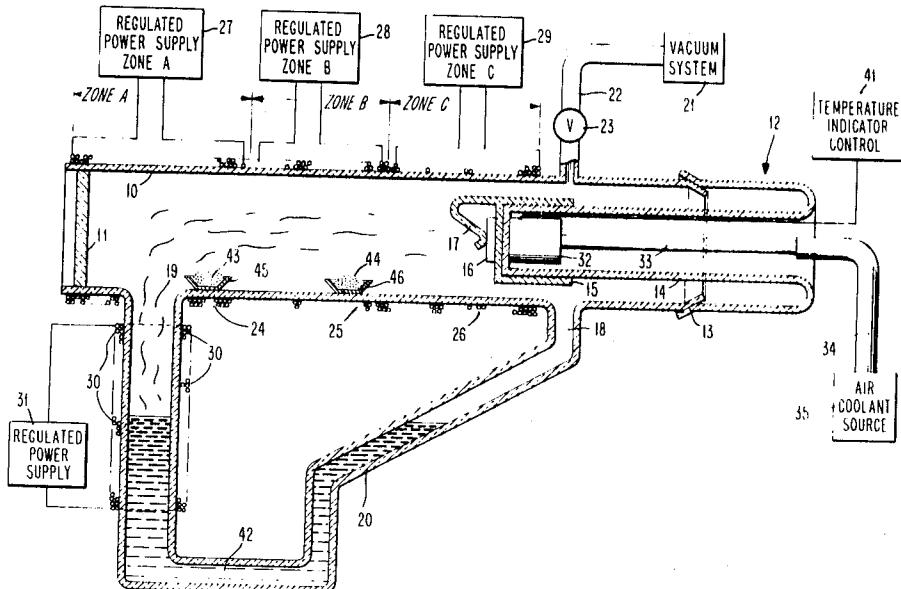
[56] References Cited
UNITED STATES PATENTS
2,759,861 8/1956 Collins 117/106 X
2,938,816 5/1960 Gunther 117/201 X
2,994,621 8/1961 Hugle et al. 117/201
3,394,390 7/1968 Cheney 23/209 X

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[54] METHOD FOR EPITAXIALLY GROWING THIN FILMS
12 Claims, 6 Drawing Figs.

[52] U.S. Cl..... 117/201,
117/106, 23/209, 252/62.3, 148/174
[51] Int. Cl..... C23c 13/08,
B05c 11/14, C23c 13/00

ABSTRACT: A monocrystalline material of the formulation $Hg_{(1-x)}Cd_xTe$ is grown epitaxially on a seed or substrate monocrystal of Cd Te, or the like. The reactants are mixed in the vapor phase and held at a temperature which prevents binary combinations. The ternary vapor phase mixture is then rapidly cooled to supersaturation and condensed on the seed crystal substrate. In a dynamic system, the mercury vapor acts as a carrier gas as well as a reactant.



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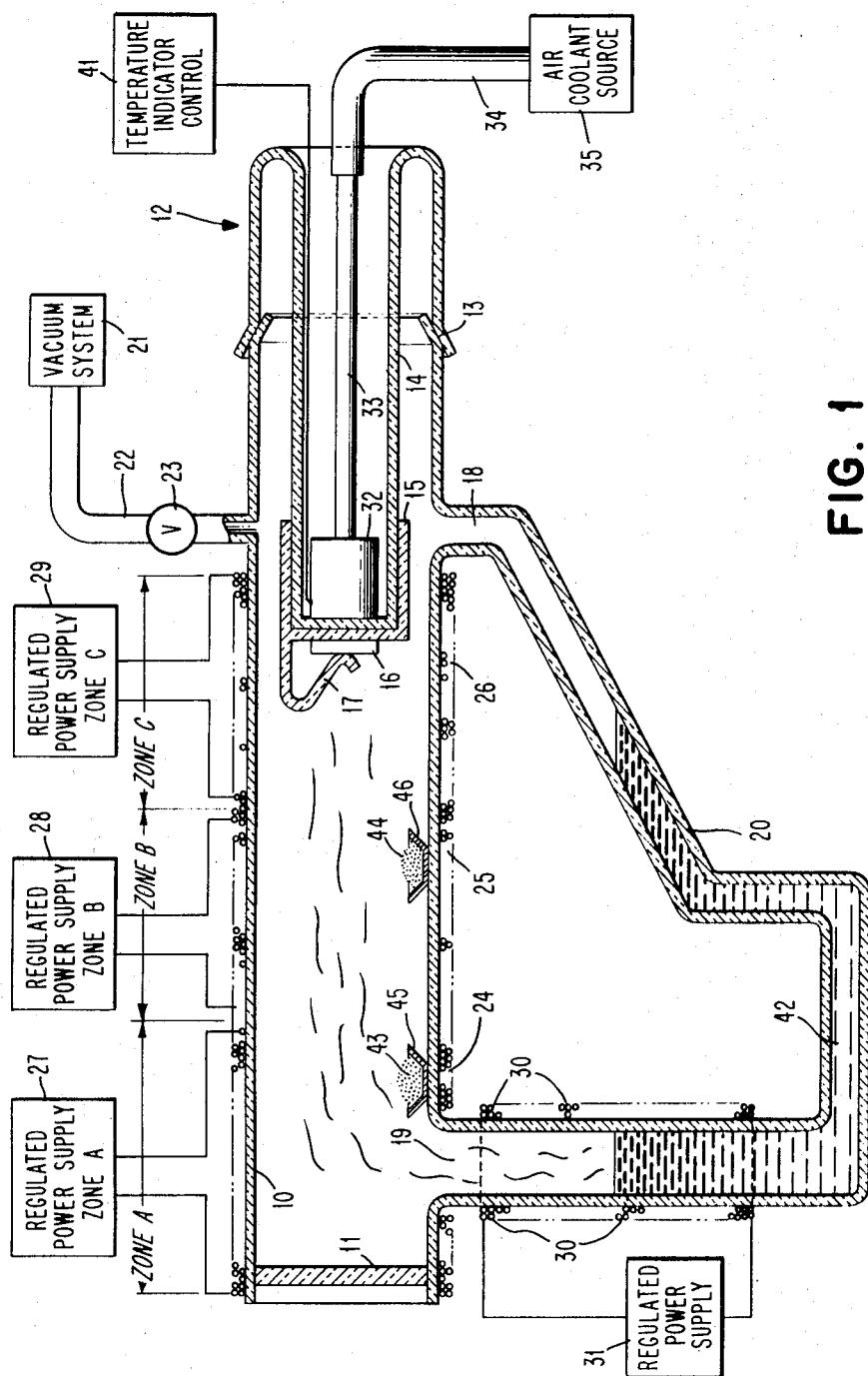


FIG. 1

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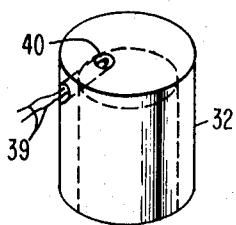


FIG. 3

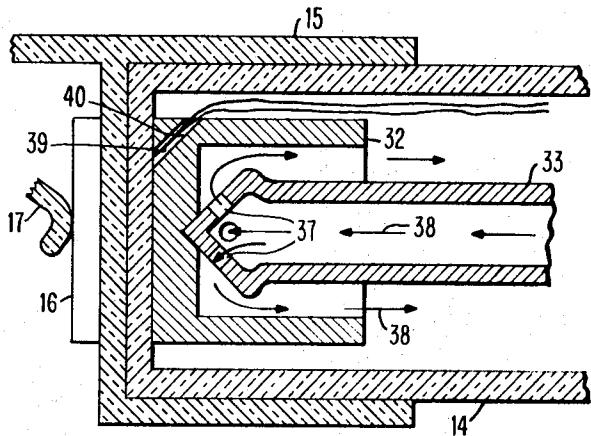


FIG. 2

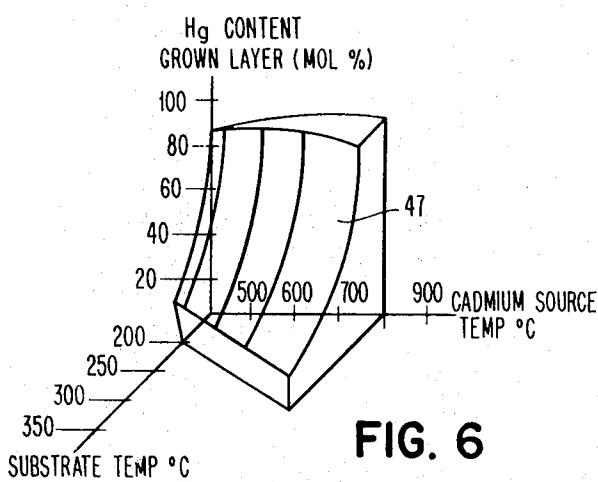


FIG. 6

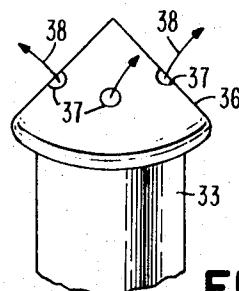


FIG. 4

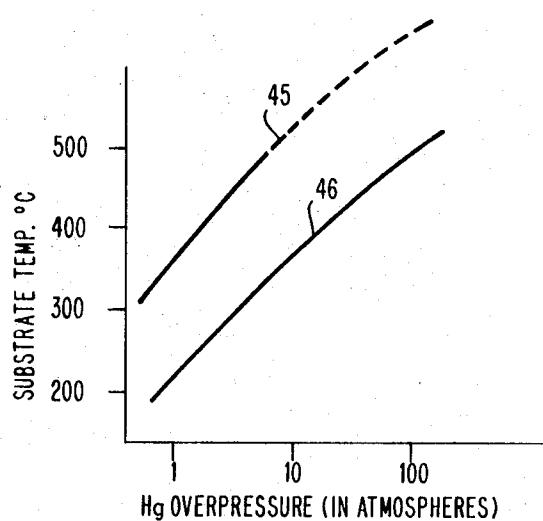


FIG. 5

METHOD FOR EPITAXIALLY GROWING THIN FILMS**BACKGROUND OF THE INVENTION**

The present invention relates to the formation of semiconductor bodies by vapor deposition and particularly to a method and apparatus for epitaxially vapor growing thin film materials of mercury, cadmium, and tellurium.

DESCRIPTION OF THE PRIOR ART

In prior processes for producing crystalline film materials from vapors of the elements and compounds of mercury, cadmium and tellurium, as well as other II-VI elements, it was thought that the presence of other vapor reactants were required to obtain growth and stoichiometric ratio control. In such processes it was common to include halogen or halogen compound vapors which produced a chemical disproportionation reaction and which acted as a transport agent for the vapor phase reactants to the growth site on a seed crystal or substrate. In such processes, the transport agent vapor condensed to some degree with the principal reactants. This tended to contaminate the end product film resulting in loss of purity and prevented the production of films having precise stoichiometric ratios.

SUMMARY OF THE INVENTION

The broad object of the present invention is to provide an improved process for epitaxially growing films from vapors of elements and compounds of materials in the II-VI valence groups.

It is a specific object to provide a process for epitaxially growing thin film crystals having the formula $Hg_{(1-x)}Cd_{(x)}Te$ where x is greater than zero and less than 1, and which has greater purity and homogeneity.

It is a further specific object to provide a process for growing monocrystalline epitaxial films of very precise stoichiometric ratio from vapors of mercury, cadmium, and tellurium elements or compounds.

The above, as well as other objects of this invention are readily achieved by vaporizing the film producing reactant materials in predetermined stoichiometric quantities in a chamber devoid of any other reactants. In the specific system for making epitaxial films having ternary combinations of mercury, cadmium, and tellurium, the mercury vapor, in addition to being a combining reactant of the end product film, also serves as the transport agent. In carrying out the process, the vapors of mercury, cadmium, and tellurium are mixed in a reaction chamber and maintained in the vapor phase at temperatures which effectively prevent preferential binary combinations. This mixture is then rapidly cooled proximate the growth site to the point of supersaturation causing a ternary reaction to occur whereby the film grown has the same stoichiometric ratio established by the composition ratio in the vapor phase. By eliminating the halogens or other disproportionation reactant vapors, and by using the vapor of one of the constituent reactants, namely mercury, as the carrier, epitaxial films were obtained having superior intrinsic properties. Preferably, the process is carried out dynamically. This is done by flowing mercury vapors through successive zones of an evacuated chamber where vaporization of the other reactants occurs and to the deposition site. Mercury is vaporized from a liquid source and excess mercury is condensed adjacent the condensation reaction region and returned to the liquid source.

The mercury recycling and redistribution acts to dynamically flow the mercury through the reaction chamber causing the reactant mixture to move more rapidly through the mixing and cooling zones to the growth site.

To achieve this dynamic system for epitaxially growing $Hg_{(1-x)}Cd_{(x)}Te$ film, the furnace apparatus is equipped with a separate recirculating conduit connected to opposite ends of the reaction chamber where vapor generation, mixing and film growing take place in a multitemperature zone. A supply of mercury is provided in liquid form in the return conduit. Heating

means is provided to vaporize the mercury for introduction at the upstream end of the reaction chamber. Individually controllable heating means is provided at successive regions along the reaction chamber for volatilizing source materials of cadmium, and tellurium, and in the region surrounding the growth site. Cooling means at the growth site is used to control the temperature of a vapor growing substrate and in combination with the heating means establishes a sharp temperature gradient in the vicinity of the substrate to provide rapid cooling.

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 view of an apparatus for epitaxially growing thin films in accordance with the present invention;

FIG. 2 is a cross-sectional view of a portion of the deposition site mechanism showing the means for cooling a deposition substrate;

FIG. 3 is an isometric view of the cooling cap of FIG. 2, showing the detail structure for using thermocouple temperature measurement;

FIG. 4 is an isometric view of the cooling probe of FIG. 2;

FIG. 5 is a graph showing the operational conditions for epitaxially growing films according to this invention; and

FIG. 6 is a three-dimensional graph for showing the operational conditions for the practice of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to FIGS. 1-4, a film growing apparatus comprises a cylindrical quartz reaction chamber 10 closed at one end by a transparent quartz wall 11 fused to the inner wall of chamber 10. The other end of the chamber 10 is inwardly tapered to receive a quartz stopper 12 outwardly tapered to coat with the chamber to produce an airtight taper joint 13. The stopper 12 has a hollow inwardly extending finger 14 to which is attached a quartz cylindrical cap 15. A substrate crystal 16 is held tightly in position against the cap 15 by a spring clip 17 which preferably is an integral part of cap 14. While only one clip 17 is shown, additional clips as well as other means may be provided, if necessary, to insure good thermal contact of the substrate 16 with cap 15. Intermediate the ends of chamber 10 are ports 18 and 19 which are connected to form a closed loop with chamber 10. When stopper 12 is in position, finger 14 extends inwardly to a position slightly beyond port 18. The chamber is evacuated by means of suitable vacuum system 21 connected through pipe 22 opened and closed by valve 23.

The reaction chamber 10 is designed to have separately controlled heating zones A, B, and C, and these are provided by suitable induction windings 24, 25, and 26 connected to suitable regulated power supplies 27, 28, and 29, respectively. A fourth heating means comprises induction coil 30 wound on conduit 20 proximate inlet port 19 and connected to a separate regulated power supply 31.

Means for temperature regulating the substrate 16 comprises metallic cylindrical heat sink 32 located within the hollow core of finger 14 and means for supplying cooling air thereto which comprises a hollow metal probe 33 connected by pipe 34 to an air coolant source 35. The probe 33 and pipe 34 are designed to be readily removable from finger 14 in order that stopper 12 may be removed from chamber 10 in preparation for the vapor growth operation. As best seen in FIGS. 2 and 4, the heat sink 32, when in position at the far end of finger 14, makes surface contact with the probe finger 14 and through cap 15 to substrate 16. The cooling probe 33 has a conical point 36 with plural apertures 37. When in position, the point of cylinder 36 makes contact with the inside of heat sink 32, and when heat sink 32 is made preferably of silver, the

point penetrates heat sink 32 thereby increasing the surface contact and holding the probe more firmly in place. Air flowing from coolant source 35, as depicted by arrows 38, exits from holes 37 into contact with the interior surfaces of heat sink 32. Cooling also is obtained by conduction from heat sink 32 to probe 33. Temperature measurement includes a thermocouple 39, or the like, with the junction located within aperture 40 of heat sink 32 and connected to indicator control means 41. When in position, the junction of thermocouple 39 is in contact with the interior wall of finger 14.

In the operation of the reaction apparatus of FIG. 1, mercury liquid 42 is placed in conduit 20 at a level whereby liquid mercury is within the heating zone of winding 30. Source material 43 and 44 in boats 45 and 46, respectively, are placed in zones A and B, respectively.

A substrate 16, is selected to grow the desired film monocrystal and after cleaning is placed in position on finger 14 and held there by clip 17. Stopper 12 is then inserted into the end of chamber 10 and maintained in place by suitable means (not shown) to maintain an airtight seal 13. Probe 33 is then inserted in finger 14 to make contact with heat sink 32 and connection by pipe 34 to coolant 35 is then completed. Upon closing of chamber 10 by stopper 12, vacuum source 21 is operated, with valve 23 open, to effect initial pumpdown of chamber 10 to remove undesirable contaminants such as water and oxygen in chamber 10. If desirable, the substrate 16 may be further cleaned by backetching. In the back-etch process, the substrate 16 is heated by coil 26 to drive off any cleaning solvent as well as some of the constituent materials of the substrate 16. These materials may be also removed by the evacuation means 21. The initial pumpdown is preferably performed after vaporization of mercury has been initiated. When the desired vacuum pressure is reached, valve 23 is closed and vacuum system 21 shut down. The heating coils 24, 35, 25, and 26, as well as coolant source 35, are activated to begin the film growth process.

In general, the growth process is practiced by heating the liquid mercury 42 causing mercury vapor to enter reaction chamber 10 through inlet port 19. Likewise, the temperatures in zones A and B are set to predetermined heat levels to volatilize the reactants from source materials 43 and 44. Due to the lower temperature at the substrate 16, caused by coolant from source 35 and in the region of finger 14, a temperature differential exists in the chamber 10 which causes mercury vapor to flow from port 19 through zones A and B, thereby producing a mixture of mercury vapor and gases of sources 43 and 44. Due to the same pressure drop, the gaseous mixture flows to zone C where the coil 26 is set to establish the temperature which prevents binary combinations in the vapor phase of the gaseous reactants. With coolant from source 35, the temperature substrate is maintained at a temperature low enough to cause the constituents of the gaseous mixture to supersaturate and condense on the surface of substrate 16.

In accordance with the present invention, the substrate temperature 16 and the temperature of the gaseous mixture in zone C are maintained at levels which provide a very sharp temperature gradient in the vicinity of the surface of substrate 16. A temperature in zone C of at least 50° C. above the substrate temperature should be maintained. Thus, the gaseous mixture experiences rapid cooling in the region close to the substrate 16 and becomes supersaturated causing the constituent reactants to condense without the aid of additional disproportionation reactants ordinarily used in such vapor growing. Throughout the entire growing process, the mercury vapor acts as a transport agent and sweeps the other reactants through the zones A-C to region of deposition. This prevents back diffusion of other reactants to port 19 and thus prevents contamination of the supply of mercury 42. The portion of the material that does not react at the growing surface is carried out of the deposition region of zone C and deposits on the walls of chamber 10 in the vicinity of port 18. The mercury vapor condensed in this region flows through port 18 back to the supply 42. Thus, the apparatus operates dynamically and

functions much as a mercury diffusion pump thereby providing a high degree of control over the process while assuring maximum purity of the mixtures to thereby achieve stoichiometry without contamination.

In practicing the present invention to produce an epitaxial film, the substrate 16 is a monocrystal carefully selected and prepared for deposition. The substrate 16 would be a material having a lattice spacing similar to that of the film to be grown. The substrate 16 is cut from monocrystal ingots previously aligned by X-ray techniques to provide a growth receiving surface along a predetermined crystallographic plane. The receiving surface of substrate 16 is then polished and cleaned.

The source materials 42 and 43 are selected from suitable crystalline materials, or the like, which are preferably pulverized to a fine degree to obtain maximum volatilization when heated. If ingot materials are used, polishing and cleaning may likewise be performed to minimize the amount of contaminants introduced into the atmosphere of chamber 10.

The following are specifications of one example of the preferred form of the present invention:

1. The substrate 16 was a Cd Te monocrystal cut from an ingot along the [100] plane. The growth receiving surface of substrate 16 was ground and polished with one-fourth micron alumina, then chemically etched in a bromine alcohol solution for 2 minutes; followed by copious alcohol rinse with subsequent drying.
2. The source material 40 located in zone A was approximately 2 grams cadmium, ground and pulverized to a fineness of 50 mesh. The source material 41 in zone B was approximately 2 grams of tellurium ground and pulverized to a fineness of 50 mesh.
3. Heat coil 30 was energized to a temperature of approximately 300° C. to generate mercury vapor and the vacuum system 21 then operated to produce initial pumpdown. When the pressure in chamber 10 reached 10 Torr., valve 23 was closed and system 21 shut down.
4. Power supply 27 and 28 were then turned on to heat coil 24 and 25 to produce a zone A temperature of 440° C., and a zone B temperature of 520° C. At the same time, power supply 29 was operated to produce a zone C temperature of 460° C. Coolant was supplied from source 35 to provide a substrate 16 temperature of 280° C. Measurement of the zone and temperatures was determined by appropriately placed thermocouples using a potentiometer recorder. For a typical run time of 1.25-2 hours under the above conditions, a stoichiometric growth layer of 7-10 mils thickness was produced whose composition was Hg 0.8 Cd 0.2 Te.

At the end of the growing process, the power to the heating coils 24, 25, and 26 is discontinued to allow cooling. The supply of coolant air is also discontinued. This prevents growth at the substrate. After cooling to room temperature the stopper may be removed without oxidation occurring on the film.

Other examples of samples and process conditions, as well as results, are set forth in the following table.

TABLE I

Sample No.	(x)		Source Temperature Hg CdTe Te	°C.	
	Hg	Cd		Hg	CdTe
MRM-142	0.8	0.2	310°	650°	430°
MRM-143	0.3	0.7	310°	500°	370°
MRM-144	0.9	0.1	310°	480°	370°
Substrate Temp. °C.	Zone C. Temp. °C.	Growth Time	Thickness		
MRM-142	260°	440°	2 Hr.	\sim 3 mils	
MRM-143	270°	445°	2 Hr.	\sim 2 mils	

MRM-144 280° 450° 2 Hr. ~ 2 mils

While the above examples are specific illustrations of actual samples, it will be appreciated that other formulations may be devised in a wide range of temperatures and concentrations in accordance with the principles of the invention. FIG. 5 shows that acceptable growth of stoichiometric film may be obtained where substrate temperatures vary within the range of 200° to 350° C. up to a range of 400° to 600° C. for a mercury overpressure of from 1 to 100 plus atmospheres. Outside of the region bounded by curves 45 and 46 the grown film no longer has a stoichiometric composition and becomes an alloy.

Other variations possible for practicing the present invention are illustrated in FIG. 6 which shows the relationship between Hg content in the grown layer to the source temperature and substrate temperature for the required molar quantity of Te. Stoichiometry is obtained in mercury cadmium telluride films for any set of conditions which fall on the curved surface 47.

While the above examples illustrate specific substrate materials for growth purposes, other crystalline materials may be used, such as HgTe, PbTe, SnTe, or the like.

Also, while the specific examples show stoichiometric film growth from elemental mercury, cadmium, and tellurium, other ternary systems in the II-VI groups could be used, such as Zn Cd Te, Zn Hg Te, Hg Cd Se, Zn Hg Se, Zn Cd Se, and the like, where Zn and Hg are the transporting agents.

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 process for the vapor growing of ternary films comprised of elements selected from the II-VI valence groups comprising:

forming a ternary gaseous mixture consisting of the vapors of said elements in a chamber substantially devoid of contaminant elements;

maintaining said ternary gaseous mixture at a reaction temperature which prevents preferential binary chemical combinations in said vapor phase whereby said mixture has a composition ratio in the vapor phase at least equal to the desired stoichiometric ratio of a film to be grown; 45

rapidly cooling said mixture to cause supersaturation and condensation of said elements on a growth substrate in the same stoichiometric ratio of said elements in said vapor phase.

2. A process in accordance with claim 1 in which said elements are mercury, cadmium, and tellurium, and said stoichiometric ratio is defined by the expression $Hg_{(1-x)}Cd_xTe$ where x is greater than zero and less than one.
- 5 3. A process in accordance with claim 2 in which said mercury, cadmium, and tellurium are separately volatilized, and said mercury vapor acts as a transport agent for said cadmium and tellurium vapors.
- 10 4. A process in accordance with claim 3 in which said mixture is maintained in the region proximate the deposition substrate at a temperature of at least 50° C. above the temperature of the substrate.
- 15 5. A process in accordance with claim 3 in which said cadmium vapor is generated from a source heated to a temperature of 440° C., said tellurium vapor is generated from a source heated to a temperature of 520° C., said mercury is volatilized with an overpressure of 30 microns, said reaction temperature of the mixture in the region proximate said substrate is 460° C. and said substrate temperature is approximately 280° C. whereby said growth film is $Hg_{0.8}Cd_{0.2}Te$.
- 20 6. A process in accordance with claim 3 in which said mercury vapor is caused to mix successively with vapors of cadmium and tellurium and to carry said mixture to a condensation reaction and vapor growth zone.
- 25 7. A process in accordance with claim 6 in which said mixing is effected by flowing a stream of mercury vapor unidirectionally from a mercury vaporization source through the vaporization sources of said cadmium and tellurium to said growth site.
- 30 8. A process in accordance with claim 7 in which said unidirectional flow is effected by controlling the temperature and pressure of the constituent vapors at the successive vaporization sources and at the growth site.
- 35 9. A process in accordance with claim 8 in which said growth site temperature and the temperature of the vapor phase mixture is controlled to regulate the stoichiometric ratio of said mixture and said film.
- 40 10. A process in accordance with claim 7 in which an excess of mercury vapor is supplied to said stream, and excess mercury remaining from the condensation reaction is collected and returned to said source of said mercury vapor.
- 45 11. A process in accordance with claim 10 in which said mercury vapor is generated from a supply of liquid mercury, and said excess mercury is distilled and returned to said liquid supply.
- 50 12. A process in accordance with claim 7 in which said mercury vapor is generated from a liquid supply, and excess mercury is condensed outside the growth site and returned to said liquid supply.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTIONPatent No. 3,619,283Dated November 9, 1971Inventor(s) Donald R. Carpenter, Gerald W. Manley,
Philip S. McDermott 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, in the "ABSTRACT", line 2,
the formula reading

$Hg_{(11x)} Cd_{(x)} Te$ should read $Hg_{(1-x)} Cd_{(x)} Te$

Column 1, line 32, the formula reading

$Hg_{(11x)} Cd_{(x)} Te$ should read $Hg_{(1-x)} Cd_{(x)} Te$

Claim 2, Column 6, line 3, the formula
reading

$Hg_{(11x)} Cd_{(x)} Te$ should read $Hg_{(1-x)} Cd_{(x)} Te$

Signed and sealed this 18th day of July 1972.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting OfficerROBERT GOTTSCHALK
Commissioner of Patents