United States Patent [19]

Kyle

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[54] **TANDEM FURNACE CRYSTAL GROWING DEVICE**

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Related U.S. Application Data

[62] Division of Ser. No. 69,025, Sept. 2, 1970, abandoned.

[52] **U.S. Cl.** ..... **23/273 SP,** 23/294, 23/301 SP

[51] **Int. Cl.** **B01j 17/26**

[58] **Field of Search** ..... 23/301 SP, 273 SP, 300, 23/305, 294

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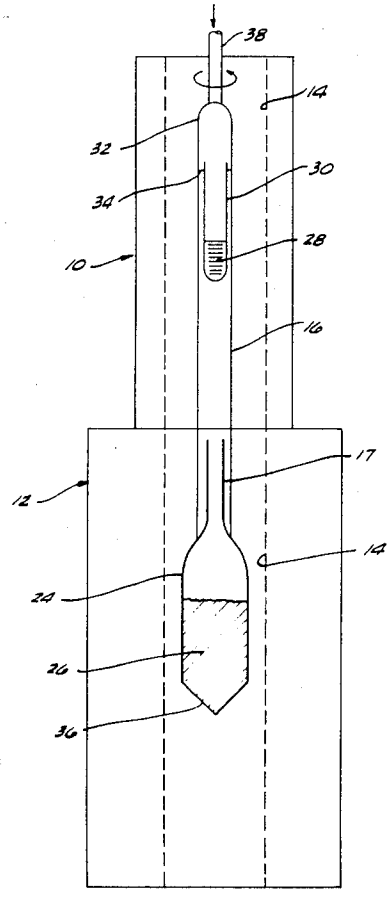
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Attorney, Agent, or Firm—James K. Haskell; Lewis B. Sternfels

[57] **ABSTRACT**

Desired conductivity type and carrier concentration in compounds in which at least one constituent is volatile can be obtained by varying the partial pressure of one of the volatile constituents with respect to the compound melt. Thus the electrical and optical properties of the Group II–VI compounds such as the sulfides, selenides and tellurides of zinc, cadmium, and mercury, the Group III–V compounds such as the arsenides, phosphides, and antimonides of gallium, indium, and aluminum, and the Group IV–VI compounds such as the sulfides, selenides, and tellurides of germanium, tin, and lead are obtained by varying the partial pressure of one compound constituent with respect to the melt.

4 Claims, 4 Drawing Figures



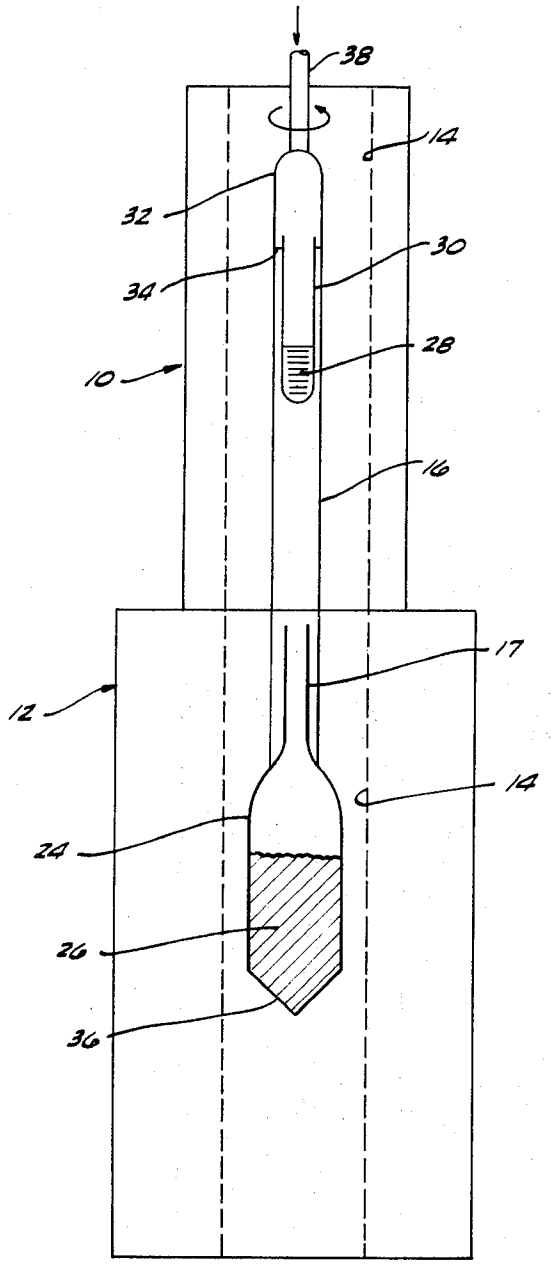


FIG. 1.

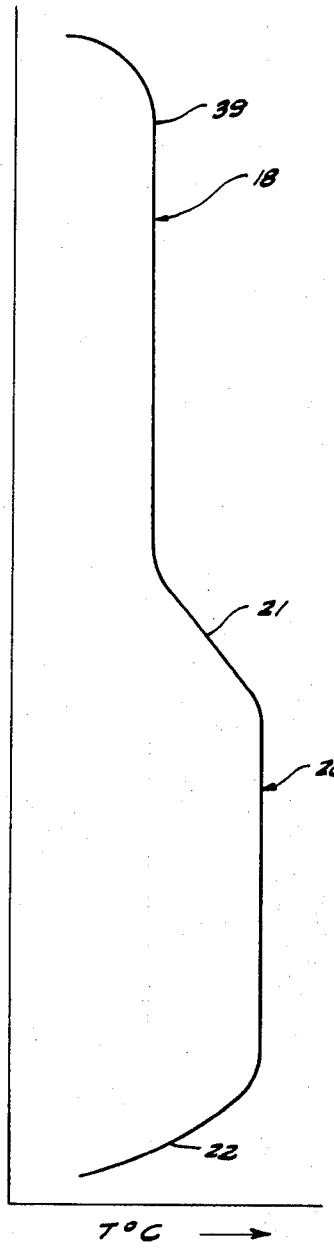


FIG. 2.

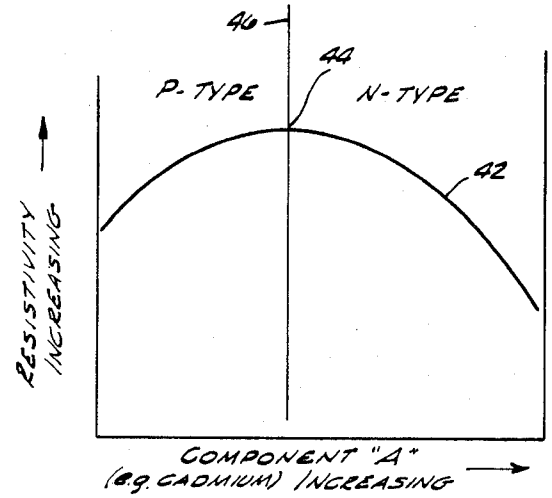

40
44
P-TYPE
N-TYPE
42
RESISTIVITY INCREASING
COMPONENT "A"
(E.G. CADMIUM) INCREASING

FIG. 3.

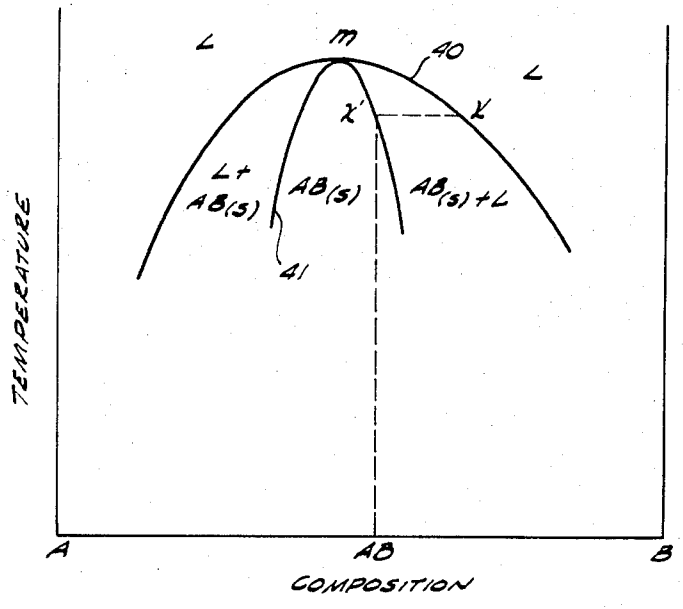

L
m
40
L
X'
X
L+
AB(S)
AB(S)
AB(S)+L
41
TEMPERATURE
A
AB
B
COMPOSITION

FIG. 4.

TANDEM FURNACE CRYSTAL GROWING DEVICE

This is a division, of application Ser. No. 69,025, filed Sept. 2, 1970, and now abandoned.

The present invention relates to a method and apparatus for obtaining desired conductivity type and carrier concentration as well as optical properties in the Group II–VI, Group III–V, and Group IV–VI compounds and, in particular, for synthesizing such compounds of a p-type, n-type, or intrinsic conductivity. Since no two compounds have exactly the same electrical, optical, or physical properties, a specific discussion of the properties of one compound does not necessarily apply directly to any other compound. For example, the melting point, vapor pressure, and equilibrium conditions for cadmium telluride cannot apply to any other compound. However, cadmium telluride is exemplatory of the inventive method hereof.

The Group II–VI compounds, for example, have found extensive use as semiconductors, radiation detectors, optical modulators, and photo sensitive devices. One compound of current interest is cadmium telluride. Much investigation has been conducted into this field, especially with respect to obtaining high resistivity compounds having at least a resistivity of 10^5 ohm-centimeters.

A foremost researcher in this field, D. de Nobel, in his Phillips Research Reports Vol. 14, pages 361–492 (1959) (see also U.S. Pat. No. 3,033,791) has shown that cadmium telluride can undergo stoichiometric deviations and that such changes in composition are caused mainly by lattice defects which determine the conductivity and type of conduction. Since cadmium telluride does show a deviation from stoichiometry, the constituents of the crystal itself can act as impurities. De Nobel's process utilizes a two step growth and diffusion or equilibrating technique under an atmosphere of one of the components in order to obtain the material with the desired electrical properties. In particular he first grew the cadmium telluride material, then cut it into small rods and re-encapsulated the rods in vacuum with excess cadmium or tellurium, and finally subjected the encapsulated materials in a furnace to equilibrate the cadmium telluride. A donor, such as indium, was utilized to make less critical the required pressure above the sample to obtain high resistivity in the cadmium telluride material.

The present invention also recognizes that cadmium telluride can undergo stoichiometric deviations and such changes in composition are caused mainly by lattice defects which determine the conductivity and type of conduction. The composition of cadmium telluride is a function of the chemical potential of one of the components when grown from the melt; therefore, it is desirable, as further recognized by the present invention, not simply to prevent decomposition of the melt, but to grow crystals of cadmium telluride under conditionos where the chemical potential of one of the components is controlled by providing a vapor of one component or constituent above the melt. The temperaturecomposition phase diagram for such a compound can be graphically represented for a two-component system (A–B) with one compound, AB, showing deviation from stoichiometry. For each point of the liquidus there is a corresponding pressure of the volatile component. If a particular pressure of the component vapor is maintained over the melt, the system has a tendency to remain at the composition corresponding to the vapor pressure applied. As solidification takes place, the segregation process tends to make the melt more and more concentrated with regard to the component present in excess; however, the liquid is no longer in equilibrium with the vapor, and a reaction between the vapor-melt occurs until the equilibrium is again attained. The end results will depend upon the rate at which the composition changes as a consequence of the segregation, as compared to the rate with which atoms are transferred between the melt and the vapor, which in turn depends on the speed of the solidifying process. Eventually a stationary state will be reached in which the crystals attain the desired composition. As a consequence, this system controls the composition of the melt, and consequently the solid, by controlling the pressure of one of the components of the melt in the vapor phase, stops decomposition of the melt, and fixes the distribution coefficients of the dopants.

The inventive process is accomplished by means of a modified Bridgman technique utilizing a novel two-part furnace. Each part of the furnace is provided with different isothermal temperature profiles. An elongated growth tube has one part in which cadmium or tellurium is placed so that it may be heated to a temperature in one of the isothermal temperature portions. In this portion, the vapor pressure of the cadmium or tellurium is controlled. In another portion of the tube, cadmium telluride is positioned and heated to the temperature of the second isothermal temperature portion, the second portion being at a temperature sufficient to create a melt from the cadmium telluride and, therefore, being higher than the temperature of the first isothermal temperature portion.

Cadmium telluride utilized in the process of the present invention is preferred to have a purity of at least 99.9999%. In the operation of the inventive process, the tempereature of the upper furnace containing the cadmium or tellurium of similar purity is adjusted so as to provide the desired pressure of cadmium or tellurium vapor. This partial pressure of the one element controls the concentration of the cadmium and tellurium ions in the melt in such a manner that the melt will be either stoichiometrically pure, cadmium rich, or tellurium rich. The tube is maintained stationary for a period of time sufficient to obtain stability of the composition of the melt. Thereafter, the tube is moved slowly through the furnace so that the melt passes through the decreasing temperature gradient and solidifies into a crystal. The isothermal temperature profile for the cadmium or tellurium in the upper part of the tube is sufficiently long so that the temperature thereof does not vary in order to insure retention of stability and the desired carrier concentration. After the last portion of the melt has been solidified, the tube is slowly cooled in a controlled manner.

It is, therefore, an object of the present invention to provide desired conductivity type and carrier concentration in Group II–VI, Group III–V, and Group IV–VI compounds of the Table of Periodic Elements.

Another object is to provide P-type, N-type, and intrinsic conductivity in such compounds.

Other aims and objects as well as a more complete understanding of the present invention will appear from the following explanation of exemplary embodi-

ments and the accompanying drawings thereof, in which:

FIG. 1 illustrates a schematic representation of a two-part furnace with a crystal growing tube therein for growth of the crystals of the present invention;

FIG. 2 schematically depicts the temperature curves of the furnaces;

FIG. 3 is a graph, not to scale, of the resistivity versus temperature-pressure curve for obtaining carrier concentration and resistivity of the crystals of the present invention; and

FIG. 4 schematically depicts the temperaturecomposition phase curve for a two-constituent compound.

Accordingly, a pair of furnaces **10** and **12** are vertically placed one atop the other or in tandem with a central opening **14** extending therethrough for placement therein and movement of a crystal growing tube **16.** A barrier **17** is positioned in the tube to act as a collector of the volatile component in case refluxing occurs. The temperature of furnace **10** is controlled so as to provide a temperature curve **18** while the temperature of furnace **12** is controlled to provide a temperature profile **20.** The temperature of furnace **10** is less than that of furnace **12** as shown in FIG. **2,** thereby producing a temperature gradient **21** therebetween. The temperature of furnace **12** is further controlled to provide a decreasing temperature gradient **22.** Furnace **10** is disposed to be at a temperature to provide a vapor pressure equal to or greater than the minimum pressure at which sublimation and/or decomposition occurs to prevent sublimation and decomposition, while furnace **12** is heated to provide a maximum temperature of above the melting point of the compound.

Tube **16** is provided with a lower section **24** in which a charge of pure II–VI, III–V, or IV–VI Group compound is placed. One constituent **28** of the compound is placed in a receptacle or reservoir **30** at another section **32** of tube **16** and secured thereto by one or more supports **34.** The preferred purity of the compound and constituent is at least 99.9999% in order to prevent the conductivity and type of material from being determined by the concentration and kind of impurities which would be otherwise present. Section **24** of the tube is terminated by a nucleation point **36** of any suitable shape, as is well known in the art. Support of section **24** may be provided or section **32** may have attached to it a rod **38** for rotating and lowering the tube through the furnace. Flat portion **39** of temperature curve **18** is maintained for a sufficiently long length so that, when tube portion **24** moves into decreasing temperature gradient **22,** constituent **28** will remain in flat temperature portion **39.**

In operation, a quantity of II–VI, III–V, or IV–VI Group compound, in compound or elemental form, which need not be stoichiometric, is placed in section **24** of tube **16** while the desired compound constituent is placed within receptacle **30** of the tube. The tube is then sealed and evacuated to approximately 10^{-8} Torr, or partially filled or pressurized with an inert gas. The tube with its contained materials is then placed within the two-part furnace as shown in FIG. **1** and the temperatures of furnaces **10** and **12** are raised to provide a melt of compound **26** and vaporization of constituent **28.** The temperature of constituent **28** at flat portion **39** is adjusted to provide a desired vapor pressure above the decomposition and/or sublimation pressure. As a consequence, a thermodynamic equilibrium is soon established between vaporized constituent **28** and melt **26** because, if the melt is deficient in the volatile component, such as cadmium, for this vapor pressure, then the component is removed from the vapor and added to the melt, and conversely, if the melt is rich in the component, then it leaves the melt as a vapor. Thus, regardless of what the composition of the melt may originally be, the composition can be reproducibly adjusted to whatever composition is desired by controlling the temperature of the vapor. For example, if constituent **28** comprises cadmium and compound melt **26** comprises cadmium telluride, an increase in the cadmium concentration in the melt will produce a correspondingly high electron concentration therein. The opposite result is obtained with a tellurium constituent as the tellurium pressure increases.

In the present invention, the pressure of the component in reservoir **30** is changed by changing the temperature of furnace **10.** For cadmium telluride, by increasing the cadmium pressure, and consequently effecting a reduction in the tellurium pressure, more cadmium is added to the system. Thus, the composition of cadmium telluride is controlled. Also, the same process would apply to tellurium. Adding tellurium would reduce the cadmium pressure, and consequently, the cadmium content.

Specifically, with reference to FIG. **4,** wherein L is the liquidus phase and S is the solidus phase of a two-component system comprising components A and B, for each point, *x*, on the liquidus-solidus interface represented by curve **40,** there is a corresponding pressure of the volatile component A or B. If a certain vapor pressure of the component is maintained over the melt, the system has a tendency to remain at the composition corresponding to the vapor pressure applied. As solidification takes place, the segregation process tends to make the melt more and more concentrated with regard to the component present in excess; however, the liquid then is no longer in equilibrium with the vapor, and a reaction between the vapor melt occurs until equilibrium is again reached. The end results of these interactions depend on the rate at which the composition changes as a consequence of the segregation, compared to the rate with which atoms are transferred between the melt and the vapor. Eventually, a stationary state is reached in which the crystals attain a composition somewhere between x′ and m in the existence region contained within curve **41.**

Because the composition of cadmium telluride is a function of the chemical potential of one of the components when grown from the melt, it is desirable to grow crystals of cadmium telluride under conditions where the chemical potential of one of the components is controlled. This is accomplished with the modified Bridgman system or technique utilized in conjunction with elongated tube **16** so that cadmium or tellurium can be placed high in the tube in receptacle **30** where its vapor pressure is controlled by furnace **10** operating significantly below the temperature of crystal furnace **12.** Thus, the properties of the compound are determined by the pressure of one of the components above the melt.

The modified Bridgman system noted above controls the composition of the melt and, consequently, the solid by controlling the pressure of one of the components of cadmium telluride over the melt, stops decom-

position and/or sublimation of the melt, and controls the distribution coefficients of the dopants.

The theory of equilibrium between solid-liquid-gas discussed herein for this system indicates that the liquid acts only as a transferring medium between gas and solid phases and, consequently, the system may be treated as a gas-solid system with respect to defect chemistry. In explanation of this theory, it is helpful to assume a model for the liquid which is equivalent to the normal crystalline model of the solid expressible as either of two types, a "gas-like" model and a "crystal-like" model. In the gas-like model, the perfect liquid is assumed to consist of molecules and dissociation products of the molecules. Ionization may occur which leads to additional imperfections. In the crystal-like model, the liquid is regarded as a crystal with an exceptionally large concentration of the Schottky-Wagner or Frenkel type defects. Intrinsic excitation and ionization are assumed to take place exactly as in a solid. Statistically both models are equivalent and give the same results.

Consequently, in the following explanation using cadmium telluride as an example where cadmium is the A component and tellurium is the B component, where x indicates an uncharged atom, α is the defect in liquid caused by the addition of Cd^x; in the liquid, β is the defect in liquid caused by removal of Cd^x from the liquid; g, l, and s are the gaseous, liquid, and solid phases, respectively, of the cadmium telluride components; P is pressure, and K is the equilibrium constant. Accordingly, $Cd_g \rightleftharpoons Cd_l + \alpha$, and for small concentrations of α,

$$K_1 = ([\alpha]/P_{Cd}). \quad (1)$$

Also, $Cd_l \rightleftharpoons Cd_g + \beta$, and for small concentrations of β,

$$K_2 = [\beta][P_{Cd}]. \quad (2)$$

Under these conditions,

$$K_{CdTe} = P_{Cd}P_{Te}^{1/2} \quad (3)$$

since $CdTe \rightleftarrows Cd_{(g)} + \frac{1}{2}Te_{2(g)}$. Accordingly,

$$[\alpha][\beta] = K_{\alpha\beta} \quad (4)$$

or the composition of the liquid is a function of P_{Cd}.

In the equilibrium between liquid and solid, the transfer of atoms from one phase to the other as well as imperfections within each phase are describable as reactions. Transfer of electrons or ions need not be considered since both phases remain neutral. If such particles are transferred, electrons and ions are transferred in equal concentrations, so that the final reactions may be expressed in terms of the transfer of neutral atoms and vacancies. Consequently, let a be a defect caused by removal of a cadmium atom from the solid. Then,

$$Cd_s^x + \beta \rightleftarrows Cd_l^x + b$$

where

Cd_s^x and Cd_l^x are unionized atoms in solid and liquid, respectively. For small concentrations of β and b,

$$K_3 = (b/\beta) \quad (5)$$

Also, $Te_s^x + \alpha \rightleftarrows Te_l^x + a$,

$$K_4 = (a/\alpha), \quad (6)$$

and

$$[a][b] = K_{ab} \quad (7)$$

With the aid of equations (4), (5), (6), and (7),

$$[a][b] = K_3K_4K_{\alpha\beta} = K_{ab}.$$

The foregoing theory was simplified by assuming that (1) the liquid is always homogeneous, (2) diffusion in the solid is slow and, therefore, the composition of the solid does not change after having grown from the liquid, (3) the gas phase equilibrium $CdTe_{(g)} \rightleftarrows Cd_{(g)} + \frac{1}{2}Te_{2(g)}$ is reached quickly with cadmium telluride molecules not present in any significant amounts, (4) the distribution coefficients are constants which are independent of composition, and (5) the solid-liquid distribution is adjusted quickly. In the modified Bridgman system described herein, the gas and solid phases are physically separated from each other by the liquid phase so that essentially the liquid phase acts as a communication medium since the composition of the liquid phase is determined by the pressure of one of the components of cadmium telluride.

The quantity of constituent **28** needed in reservoir **30** is not critical since the pressure is determined by the temperature of the reservoir and is independent of the amount of material in the reservoir. Of course, if insufficient material were placed in the reservoir, then obviously the required pressure could not be obtained. The exact amount can be determined from a pressure-temperature-composition phase diagram; however, in actual practice, simply more constituent is used than is required.

As an aid to understanding the method by which a particular electrical characteristic, in terms of resistivity, and the carrier type of the crystal is obtained, reference is made to FIG. **3.** Curve **42** represents the resistivity curve for cadmium telluride which is representative of some II–VI, III–V, or IV–VI Group compound crystals having either a P-type or an N-type nature. A maximum resistivity occurs at point **44** of curve **42.** To the left of a line **46** passing through point **44,** the crystal is P-type while to the right of line **46,** the crystal is N-type. As the crystal becomes more P-type or N-type, the resistivity decreases. Each point of resistivity corresponding to the degree of P-type or N-type concentration is determined by the pressure of the crystal constituent. Thus, as the melt composition moves toward the right hand side, that is, toward the "N-type" area, so also does the solid composition move and the electrical properties will accordingly vary. Furthermore, to obtain the particular electrical characteristic, the compound composition must remain a constant. By using a reservoir supply, the melt composition can be kept constant, thus insuring a constant solid composition. For cadmium telluride and the cadmium constituent, as the temperature **18** of furnace **10** increases, the cadmium pressure also increases, thereby increasing the conductivity. The same analysis is true when the cadmium pressure is allowed to decrease toward the left of the figure in order to obtain a "P-type" semiconductor material. The further to the left the composition moves in accordance with decreased cadmium pressure, the lower the resistivity becomes. Therefore, the temperature and pressure of the cadmium constituent are so controlled as to obtain a point just to the left or right of the highest resistivity characteristic at point **44.**

Therefore, the pressure of the compound constituent is closely controlled so as to obtain the desired resistivity. Initially, the tube and its contained materials are maintained stationary within furnaces **10** and **12** for a period of time sufficient to obtain stabilization of car-

rier concentration under the adjusted temperature-pressure parameters of the system. Thereafter, tube **16** is lowered through the furnaces by means of rod **38** at a rate appropriate to nucleation of the particular compound, e.g., approximately 0.20 inches per hour for cadmium telluride, so that nucleation tip **36** passes through the decreasing temperature gradient **22** in order to solidify the melt into a single crystal as it passes through the liquid-solid plane of the decreasing temperature gradient. The length of furnace **10** and its uniform temperature curve **18** is maintained long enough so that the temperature, and therefore, the pressure of constituent **28** will not vary and thereby will not affect the constituent vapor pressure.

The following table lists examples of materials prepared by use of the describeid method:

Reservoir Temperature C°	Atmosphere Above Melt	Pressure (Atmospheres)	Type Crystal	Resistivity Ω-cm
768	Cadmium	0.9	*	2×10^8
768	Cadmium	0.91	*	1×10^8
768	Cadmium	0.91	*	$10^7 - 10^8$
860	Cadmium	2.6	N	3.5
860	Cadmium	2.6	N	5.0
917	Tellurium	0.51	P	100.0

*Conductivity type of high resistivity material was not practically possible to determine and was uncertain. Theoretically, it is P-type but could border N-type; thus, it is intrinsic.

Although the invention has been described with reference to a particular embodiment thereof, it should be realized that various changes and modifications may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. An apparatus for obtaining desired conductivity type and carrier concentration in semiconductor crystal compounds selected from one of the II–VI, III–V, and IV–VI Groups of the Periodic Table of Elements comprising:

a pair of furnace means placed in tandem and having central opening means extending therethrough, each of said furnace means having means for providing elongated isothermal temperature portions of specified lengths and for providing a decreasing temperature gradient terminating the first of the isothermal temperature portions and passing through the crystallization temperature of the selected compound;

means for positioning a crystal growth tube in and moving said tube through said central opening means, said tube comprising first and second sections and means for attaching said sections together,

said first section having means for containing the selected Group compound, said first section being placeable within and movable through the first of the isothermal temperature portions and the decreasing temperature gradient by said positioning and moving means, and

said second section having means for containing one constituent of the selected Group compound, said second section being placeable within and movable only within the second of the isothermal temperature portions by said positioning and moving means said first and second containing means having a specified distance therebetween,

the length of the second isothermal temperature portion being at least as long as the combined length of the first isothermal temperature portion and the decreasing temperature gradient and being at least as long as the specified distance between said first and second containing means, and the said containing means of said second tube section remaining within the second isothermal temperature portion when the containing means of said first tube section moves through the first isothermal temperature portion and the decreasing temperature gradient.

2. An apparatus as in claim **1** further including a reservoir secured within said second tube section for receiving the one constituent.

3. An apparatus as in claim **1** further including barrier means secured to the interior of said tube within said spacing means and intermediate said first and second tube sections for collecting refluxed volatile constituent.

4. A crystal growth tube closed from the external environment for use in synthesizing crystal materials comprising:

a first section for nucleating the crystal materials;

a second section for receiving at least some materials to be nucleated and spaced from and physically above said first section;

spacing means separating said first and second sections; and

means for defining a barrier secured to the interior of said tube within said spacing means, intermediate said first and second tube sections, and opening towards said second section for collecting refluxed material.

* * * * *