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METHOD OF GROWING CHALCOGENIDE PSEUDO-BINARY CRYSTALS OF UNIFORM COMPOSITION

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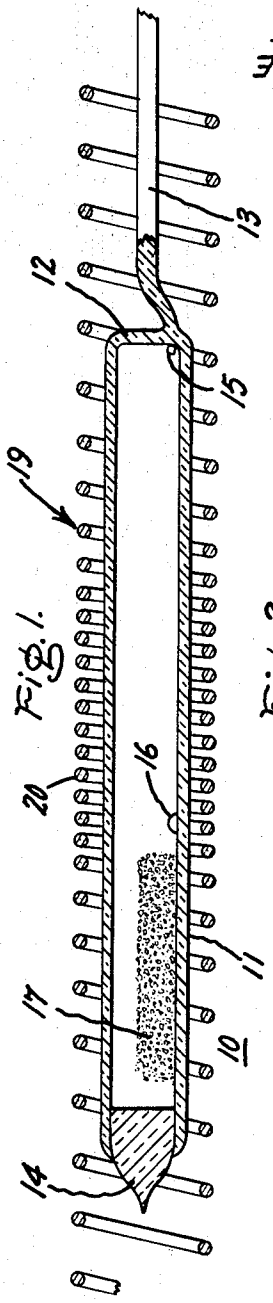


Fig. 1.

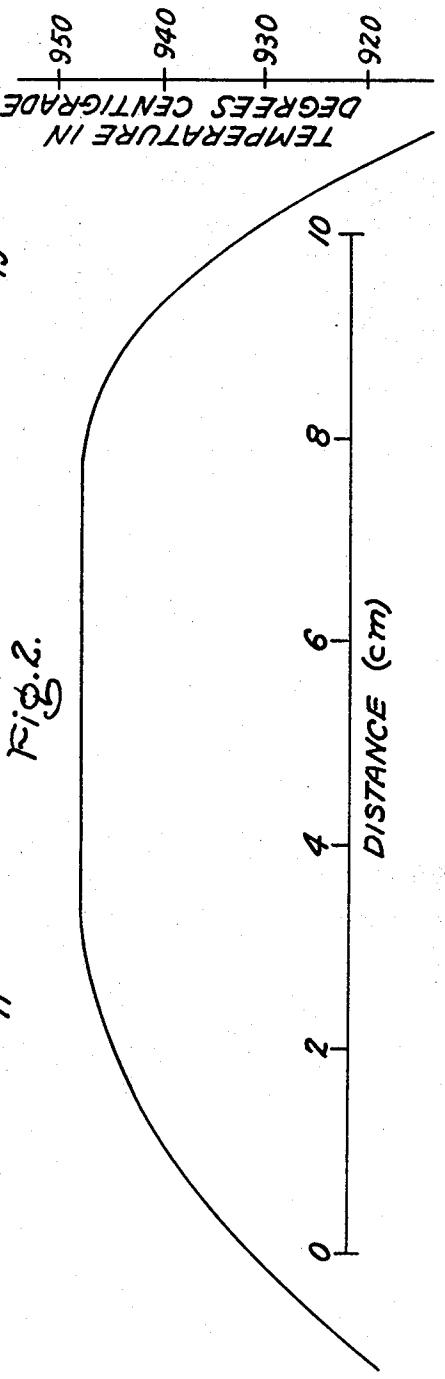


Fig. 2.

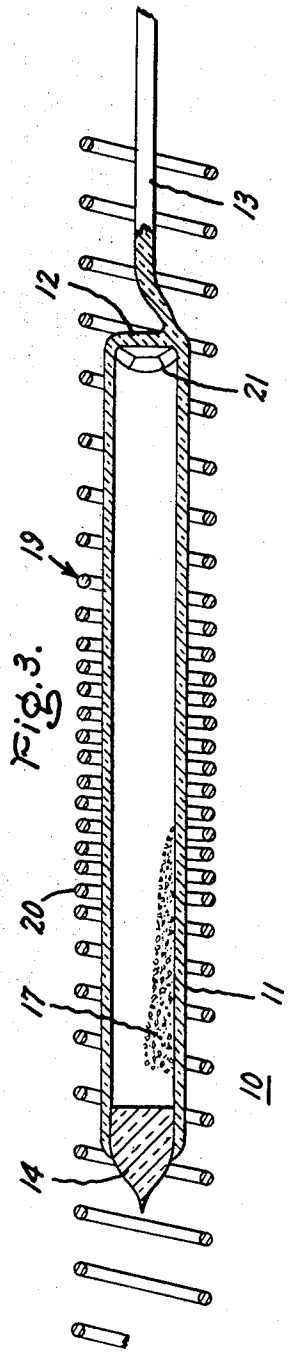


Fig. 3.

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METHOD OF GROWING CHALCOGENIDE PSEUDO-BINARY CRYSTALS OF UNIFORM COMPOSITION

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U.S. Cl. 148—1.6 8 Claims

ABSTRACT OF THE DISCLOSURE

A method of growing single or near single crystals of pseudo-binary compounds of the chalcogenide type includes the growing of crystals in a sealed envelope with a charge of the chalcogenide at a preselected temperature to cause volatilization thereof and condensation of the compound upon a seed crystal or growth therefrom maintained at a temperature only slightly cooler than the temperature of the charge. To prevent segregation of the binary compound which is the most volatile of the individual binary compounds of the complex compound at one end of the envelope, a partial pressure of the anion of the most volatile binary compound is maintained within the closed envelope.

The present invention relates to a method for the growth of complex crystals of chalcogenide compounds wherein a complex anion is present. More particularly, the invention relates to growth of such crystals by a method which avoids segregation of one binary compound of the complex binary solid solution along the length of the growth tube. The invention disclosed herein was made under government contract or under a contract or subcontract thereunder with the Department of the Air Force.

Chalocogenides, principally sulfides, selenides, and tellurides, of Group II metals of the Periodic Table of the elements, particularly, zinc and cadmium, have proven to have great utility as luminescent materials, as photoconductors, and as having a wide variety of uses in semiconductive devices wherein a wide band gap is desired. More recently, it has been discovered that mixed compounds, generally defined as pseudo-binary compounds, of the type described herein, have particularly useful characteristics. Thus, for example, by providing a mixed cation, the luminescent emission of the material may be provided with a variety of spectral distributions. Similarly, by providing a material with a complex anion, greater versatility with respect to band gap and the ability to attain various types of electrical conductivity has been achieved. Thus, for example, in the copending application of M. Aven and W. Garwacki, Ser. No. 624,384, filed Mar. 21, 1967, and assigned to the present assignee, it has been disclosed that homojunctions between differently-doped regions of a zinc seleno-telluride having the generallized formula $ZnSe_xTe_{(1-x)}$ may be provided. This overcomes a great need in the art for homojunctions in chalcogenide compounds since, it had previously been possible to obtain N-type material only with certain chalcogenide materials and P-type materials with certain other chalcogenide materials. Due to this limitation, a chalcogenide P-N junction device generally previously utilized a heterojunction, with a first chalcogenide having N-type conductivity juxtaposed adjacent a chalcogenide having P-type conductivity characteristics. As used herein the term "pseudo-binary chalcogenide compound" is intended to mean a chalcogenide compound having a complex anion containing at least two chalcogens.

The characteristics of a chalcogenide, as any other semiconductor, depends greatly upon the method of fabrication and growth and, to a very large extent, upon the method of growth of a monocrystal from which highly-purified wafers are produced. In the production of true binary chalcogenide compounds such as zinc sulfide, zinc selenide, zinc telluride, and the corresponding cadmium compounds thereof, it has been relatively simple, in accord with teachings of the prior art, to grow single crystals of a substantial size such as to permit the fabrication of useful devices from wafers cut therefrom. In the fabrication of such devices, uniformity is obtained by now well-known processes. See, for example, W. W. Piper and S. Polich, Journal of Applied Physics, 32, 1278 (1961).

In the formation of pseudo-binary chalcogenide compounds, on the other hand, the provision of crystals having uniform composition throughout is an exceedingly complex and difficult matter. This is due largely to the fact that a complex chalcogenide compound, as for example, zinc seleno-sulfide, may be considered as a solic solution of zinc selenide and zinc sulfide. In the growth of a monocrystalline wafer of such a material, it is necessary to place a charge of the material in one portion of an evacuated, or near evacuated, closed reaction tube or chamber, to heat the same to cause volatilization to the vapor phase, and cause condensation, from the vapor phase, upon a colder portion of the bulb wall, or upon a seed crystal, in the form of a single crystal, which is propagated by epitaxial growth to form a large monocrystal of the compound.

In processes such as that described briefly hereinbefore, a problem in maintaining uniformity of the crystal arises, in that one individual binary compound comprising the complex chalcogenide very often has a different vapor pressure at a given temperature and may volatilize from the charge at a greater rate than the other compound, thus causing the vapor phase to have a composition which is not representative of the composition of its constituents in the solid phase. This is particularly characteristic of pseudo-binary chalcogenides containing a complex anion in which one of the constituents thereof is tellurium, inasmuch as tellurium compounds, such as zinc telluride and cadmium telluride, are exceedingly volatile as compared to the corresponding sulfides and selenides.

Accordingly, it is a principal object of the present invention to provide an improved method for the formation of uniform crystals of pseudo-binary chalcogenide compounds.

Still another object of the present invention is to provide methods for reproducibly controlling the characteristics of vapor phase epitaxial growth of pseudo-binary chalcogenide compounds.

Still another object of the present invention is to provide crystals of pseudo-binary chalcogenide compounds, particularly those containing tellurium, having uniform composition throughout the crystal.

Briefly stated, in accord with one embodiment of the present invention, we form large single crystals of chalcogenide pseudo-binary compounds, having tellurium as one member of a complex anion thereof, by placing a seed crystal of the compound having the desired composition in one end of an evacuable envelope, placing a charge having the same composition in the opposite end of said envelope, placing therein a quantity of elemental tellurium sufficient to cause a near saturation vapor pressure of tellurium therein at the operating temperature and sealing off the envelope, after evacuation. During a heating cycle of operation, the tellurium is completely vaporized and the presence thereof within the envelope causes the composition of the vapors in the vicinity of the growing crystal to

be essentially that of the charge throughout the growth cycle, so that the grown crystal is of the same composition as the charge and is substantially uniform in composition throughout its length.

The novel features believed characteristic of the present invention are set forth in the appended claims. The invention itself, together with further objects and advantages thereof, may best be understood with reference to the following detailed description, taken in connection with the appended drawing in which:

FIG. 1 is a vertical cross-sectional schematic view of a crystal growth envelope and an associated heating element therefor, containing a charge of a pseudo-binary chalcogenide in accord with the present invention, prior to the growth thereof.

FIG. 2 is a plot of a typical temperature profile which is utilized in connection with the growth apparatus of FIG. 1, and

FIG. 3 is a vertical schematic cross-sectional view of the apparatus of FIG. 1 during growth of a crystal.

FIGS. 1, 2, and 3 of the drawing are drawn with an inter-relation to one another, such that the temperature profile established in FIG. 2 is that which is applied to the growth tube of FIG. 1 in its position relative thereto. Similarly, the temperature profile of FIG. 2 is that which is applied to the growth tube of FIG. 3 in its position relative thereto.

In FIG. 1, a crystal growth apparatus, represented generally as **10**, includes a long cylindrical quartz tube **11** having a first closed end **12** to which is attached an elongated support and heat sink member **13** which contacts, and is a part of, the closed portion **12** of tube **11** only at a specific position at the lower section of the tube as it is positioned in a horizontal position. The opposite end of tube **11** is open, but may be closed with a quartz plug **14**, after filling. In the practice of the present invention, quartz tube **11** is prepared by the placing of a seed crystal **15** at the closed end thereof immediately adjacent the portion of end wall **12** at which heat dissipating member **13** abutts the end thereof. To complete the filling of the tube, a charge of elemental tellurium **16** is inserted within the tube and a charge **17** of the pseudo-binary chalcogenide compound which is to be grown in monocrystalline form is placed near the closeable end of the tube. Quartz plug **14** is placed in position and is fused into the open end of the tube. The tube is evacuated by a "tip-off" (not shown) to a pressure of approximately 10^{-5} torr and the "tip-off" is sealed. The tube is then ready for insertion into a temperature profile-establishing furnace represented by helical heater coil **19**, having a plurality of windings **20** which are concentrated at the center portion thereof, to give a high and relatively-constant temperature over the greater portion of the tube. The windings **20** of coil **19** are gradually spaced farther and farther apart, away from the center thereof, to allow the temperature profile to "fall" at either side of the central portion, establishing a profile such as that illustrated in FIG. 2.

In FIG. 2, a typical temperature profile for a 10 centimeter long reaction tube is illustrated as rising gradually from a value of approximately 920° C., at either end to a maximum value of approximately 940° C., at which it stabilizes over the greater portion thereof.

In practicing the process of the present invention, tube **11** is filled, as is described hereinbefore. Tube **11** is then positioned within the heater, as is illustrated in FIG. 1, having the temperature profile which is achieved by correlating FIG. 1 and 2. It may be noted that, with this positioning, seed crystal **15** is at substantially the maximum temperature, whereas charge **16** is only partly at this maximum temperature and is partly at a reduced temperature. During the initial portion of the first step of this process, the objective is to first thermally etch the seed crystal **15** by causing a portion thereof to vaporize to present a clean surface ready for nucleation of epitaxially-grown crystal material thereupon. At this time, it is not necessary or particularly required, that the material of the charge be volatilized to any great extent, since growth does not occur at this point, although as a practical matter such vaporization does occur. Crystal growth is prevented at this time, utilizing this interrelation between the reaction tube and the temperature profile, because the temperature of the crystal, according to the utilization of the temperature profile, is slightly in excess of the average temperature of the charge and generally may be of from 2 to 10 degrees centigrade in excess of the average charge temperature. With these conditions, the direction of the equilibrium exchange of crystal at the seed crystal is for solid material of the seed crystal to be vaporized rather than for gaseous material to be condensed, as is the condition during crystal growth.

After the crystal has been etched sufficiently, and typically may be etched until approximately 25 to 30 percent thereof is removed, which etching may be achieved in approximately one half hour, utilizing the temperature profile and the juxtaposition of the crystal growth tube as is illustrated in the correlation of FIGS. 1 and 2, the process is ready for the crystal growth stage.

Crystal growth is initiated by repositioning the crystal growth tube **11** to a position as is illustrated in FIG. 3 of the drawing. Correlating FIG. 3 with FIG. 2, it may be seen that the seed crystal is now maintained at a temperature which is slightly lower than the average temperature of the charge from which the vapor which condenses upon the growing crystal is derived. Typically, this temperature differential may be from 2 to 10 degrees centigrade and is preferably approximately 5 degrees centigrade. Since the charge of elemental tellurium within the envelope is at the higher temperature profile portion of the envelope and, since the vapor pressure of tellurium at this temperature is sufficiently high, the tellurium is evaporated completely. The amount of tellurium within the tube is chosen so as to supply a partial pressure of tellurium pressure within the crystal growth tube of from approximately 5×10^{-1} atmospheres to approximately 5×10^{-2} atmospheres. Since these values are lower than the saturation vapor pressure for tellurium at the temperature utilized, the quantity of tellurium is chosen in accord with the volume of the crystal growth tube so as to provide only sufficient tellurium to produce the desired partial pressure thereof.

As is mentioned hereinbefore, when a simple binary chalcogenide compound is vaporized and grown upon a seed crystal in apparatus similar to that illustrated herein, the composition of the vapor phase in the immediate vicinity of the growing crystal is the same as the composition of the charge from which the vapor is formed. Consequently, the growing crystal accurately reflects, and in uniformly representative of, the composition of the charge. A complex chalogenide which is a pseudo-binary compound, such as, for example, zinc seleno-telluride, is in realty a solid solution of zinc selenide and zinc telluride. When this material is heated and vaporized, the individual constituents enter the vapor phase in accord with their individual vapor pressure characteristics. Since zinc telluride is much more volatile than zinc selenide, the rate of vaporization of zinc telluride is much greater than that of zinc selenide. If no precaution were taken to counteract this effect, the proportion of the vapor in the immediate vicinity of the growing crystal at the seed crystal end of the growth tube would be exceedingly rich in concentration of tellurium and poor in concentration of selenium. Accordingly, the seed end of a growing crystal would be predominately zinc telluride and the value of x in the formula $ZnSe_xTe_{(1-x)}$ would be relatively small at the beginning of the growth cycle. As however, the zinc telluride is depleted from the vapor phase and as a substantial portion of the charge becomes volatilized, the concentration of zinc telluride, as compared with that of zinc selenide in the vicinity of the growing crystal would decrease, so that, at the end of the growth cycle

the value of x in the aforementioned formula would be substantially higher than that at the beginning of the cycle.

The foregoing problem has made it difficult in the past to grow uniform crystals of pseudo-binary compounds of chalcogenides. Some expedients have been attempted in order to avoid this disadvantage. One expedient which has been attempted has been the addition of a pressure of an inert gas such as argon to tend to reduce the rapid volatilization of the more volatile component. This expedient, although decreasing the disparity between the values of x at the beginning and end of the grown crystal, has proved substantially ineffectual to produce uniform crystals.

In accord with the present invention, we have found that the disparity between the values of x in the formation of pseudo-binary chalcogenide compounds such as represented by the aforementioned formula may be achieved, particularly in compounds in which tellurium is part of the complex anion, by the addition of a quantity of free elemental tellurium sufficient to yield a specific and operative pressure of tellurium within the growth tube that is in excess of any vapor pressure of tellurium due to the vaporization of zinc telluride from the charge. While there is some theoretical basis for belief that the addition of the anion of the less volatile simple chalcogenide would be useful in this respect, theory indicates that the quantity would be very small and accurate control thereof quite difficult. We have found that the partial pressure of tellurium required to effectuate this change is within the range of approximately 5×10^{-2} to 5×10^{-1} atmospheres of tellurium. It is important that only a sufficient quantity of tellurium be added to produce the desired range since, if excess tellurium is added and a saturated volume thereof is obtained within the growth tube, such a pressure is of the order of a partial pressure of approximately 0.6 atmosphere. This pressure of tellurium is found experimentally to be of such an excessive value that it greatly retards the growth rate of a growing crystal within the tubes presently used. Since, however, the growth rate is believed to be limited by diffusion of the vapor along the reaction tube, and since diffusion is a function of tube cross sectional area, it is possible that even a saturated quantity of tellurium may be used with very large diameter tubes.

The practice of the present invention may be conducted utilizing apparatus as is illustrated in FIGS. 1 and 3 as having a quartz reaction tube of approximately 8 centimeters in length and approximately 0.2 to 1.5 and preferably, 1.0 centimeters in diameter. The starting material for a typical charge to form a zinc seleno-telluride may conveniently be zinc selenide and zinc telluride of reagent grade, which may conveniently be obtained from Eagle Pitcher Company, for example. The powders are weighed out in the desired proportion, as for example, 5.72 grams of zinc telluride and 4.28 grams of zinc selenide for a mixture corresponding to [x=0.3]. The powders are dry mixed and passed a few times through a 90-mesh silk screen and prefired at approximately 850° C. in flowing pure dry hydrogen for one to two hours. Although dopants such as lithium or phosphorus may be added to the powdered mix, this is not necessary unless such additions are desired. The powders are sintered at temperatures of approximately 925° C. to 1025° C. for from 60 to 80 hours, increasing the bulk density of the prefired powder from about 40 percent to about 80 to 95 percent of the bulk density of the grown crystal. The sintered powdered compact is then transferred to a growth tube wherein a zinc seleno-telluride seed crystal, for example having a value of x of between 0.3 and 0.7, is placed. The seed crystal is placed in the desired crystallographic orientation, for example, with the (1,0,0) plane facing the charge. For a reaction tube having a volume of, e.g., 8 cm.^{3}, 0.0003 gram of elemental tellurium are added to the reaction tube near the charge. The tube is then plugged and fused closed at the open end, evacuated to a pressure of approximately 10^{-5} mm. of mercury and sealed off to vacuum. The tube is then placed in the heater coil and the temperature adjusted so that the temperature maximum of the profile imposed thereupon is approximately 925° C., with the positioning achieved by correlating FIGS. 1 and 2. The seed crystal, being located at a point at which this maximum occurs, is at the temperature of 925° C. as illustrated by the position of the reaction tube in FIG. 1. Since the charge of the mixed zinc selenide and zinc telluride is at a lower temperature, approximately 7° cooler, vaporization thereof may occur, but no condensation of the vapors upon the seed crystal occurs.

After approximately 30 minutes of thermal etching of the seed crystal, the tube **10** is removed to the position indicated in FIG. 3 relative to the temperature profile of FIG. 2. In this position the seed crystal is at a temperature of approximately 920° C., while the temperature of the charge raises to an average temperature of approximately 925° C. and the temperature of the elemental tellurium is approximately 925° C. Under these conditions the tellurium is entirely vaporized and establishes within the tube a pressure of approximately 10^{-1} atmospheres thereof. Simultaneously, the charge begins to evaporate and builds up a stabilized pressure thereof within the tube, which is the equilibrium partial pressure of the materials at that temperature. Under these conditions, nucleation of zinc seleno-telluride, substantially having the same value of x in the formula thereof, as in the seed crystal and in the charge, taken as a whole, occurs and the crystal orientation of the seed crystal is propagated epitaxially to form a large single crystal of zinc seleno-telluride which grows at a growth rate of approximately 100 milligrams per day, for example, (in a 0.7 cm. diameter tube). After 150 to 250 hours of growth under these conditions, most of the charge has evaporated and a monocrystal of zinc seleno-telluride having a uniform composition and a length of approximately 0.3 centimeter and a diameter of approximately 0.7 centimeter is formed in the seed crystal end of the reaction tube. Approximately ¼ to ⅓ of the charge is not vaporized, so that nonvolatile impurities may be kept out of the growing crystal.

As examples of the uniformity of crystals grown in accord with the present invention, as compared with crystals grown under identical conditions, utilizing the same method but without the pressure of excess tellurium, in accord with the present invention, are as follows. In one run a uniform starting charge, 0.75 gm. of zinc seleno-telluride, having the formula $ZnEe_xTe_{(1-x)}$ wherein x had a value of 0.30 with a pressure of 5×10^{-2} atmospheres of tellurium, measuring a sample taken from the beginning of a 1.2 centimeter long crystal with a diameter of 2 millimeters, it was found that, after stopping the reaction after the growth of a 1.2 cm. of crystal, the value of x in the remaining portion of the charge was 0.31 whereas the value of x at the beginning of the grown crystal was 1.28 and the value of x at the end of the grown crystal was 0.29. In another run a charge of 1.5 grams was used, as was a pressure of 5×10^{-2} atmospheres of tellurium and the reaction run to completion, growing a crystal 3 millimeters in length and 7 millimeters in diameter. The value of x at the top of the crystal was 0.30, and at the bottom of the crystal was 0.31.

As a control another charge of 0.75 gm. without any tellurium atmosphere was run and a 1.2 centimeter long crystal having a diameter of 2 millimeters was grown from a charge having the value of x of 0.30. At the completion of that portion of the run, the value of x in the remaining portion of the charge was 0.78 whereas the value of x at the beginning of the crystal was 0.09 and at the end of the crystal was 0.26.

As a similar control utilizing a charge of 0.75 gm. having initial value of x of 0.55 and growing a 1.2 millimeter long crystal having a diameter of 2 millimeters

and stopping the reaction, with a pressure of 5×10^{-2} atmospheres of argon within the reaction tube rather than tellurium, it was found that the value of x at the beginning of the crystal was 0.32 and at the end of the crystal was 0.25.

From the foregoing, it may be seen that substantial uniformity is attained when practicing the growth of pseudo-binary chalcogenide crystals in accord with the techniques of the present invention. While the specific examples hereinbefore have been given with respect to certain examples, they are not to be utilized in a limiting sense. Crystals may be grown in accord with the present invention using simple or complex cations, such as for example, zinc, cadmium, or mixtures thereof and utilizing anions of selenium, sulfur, and tellurium or mixtures thereof, although the greatest advantages of the invention are attained when tellurium is one of the constituents of the anion since tellurides have the greatest disparity from selenides or sulfides, when in a chalcogenide compound with a cation such as zinc or cadmium, as far as vapor pressure is concerned.

From the foregoing it may readily be seen that we have devised a new and improved method for the formation of pseudo-binary chalcogenide compounds in single crystalline form which makes possible the growth of large single crystals having uniform composition, even though the constituents thereof have vastly different volatilities. As used herein the term "single crystal" is used to connote a large monocrystalline ingot having a diameter of one to 15 millimeters and a length of at least 0.2 to 12 centimeters and having a homogeneous and uniform crystal lattice structure. This is as opposed to the formation of a plurality of crystals or an ingot consisting of polycrystalline material. This distinction is well known to those skilled in the art.

While the invention has been set forth herein with respect to certain specific embodiments and examples thereof, many modifications and changes will occur to those skilled in the art. Accordingly, by the appended claims we intend to cover all such modifications and changes as fall within the true spirit and scope of the present invention.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. A method of growing large crystals of pseudo-binary chalcogenide compounds having uniform composition which method comprises:

(a) placing a charge of a pseudo-binary chalcogenide compound comprising a plurality of binary chalcogenide compounds, at least one of which is more volatile than another thereof and a quantity of elemental chalcogen of said more volatile binary chalcogenide compound at a first end of a reaction envelope, and a seed crystal of said pseudo-binary chalcogenide compound at a second end of said envelope;

(b) evacuating said envelop to a pressure of approximately 10^{-5} torr at substantially room temperature and hermetically sealing said envelope;

(c) subjecting said envelope to a first temperature profile wherein said charge is heated to a temperature sufficient to cause the establishment of a substantial vapor pressure thereof within said envelope, and said seed crystal is heated to a higher temperature at which it is thermally etched to provide an ideal nucleation surface thereon but does not completely evaporate;

(d) altering the temperature within said envelope to subject said charge and said elemental chalcogen to a second temperature sufficient to cause volatilization thereof to occur, and said seed crystal is heated to a temperature which is lower, but only slightly less than the temperature of said charge and is at the coldest portion of said envelope so that said compound nucleates thereupon and said crystal is grown by epitaxial growth from the vapor state,

(d_1) said second temperature and the quantity of elemental chalcogen being of such values that all of said elemental chalcogen is vaporized and establishes a partial pressure thereof in said envelope sufficient to insure the condensation of said compound upon said growing crystal with the same proportion of elemental chalcogen in the anion thereof as is present in said charge.

2. The method of claim 1 wherein said chalcogenide pseudo-binary compound has a cation selected from the group consisting of zinc and cadmium and mixtures thereof and a complex cation containing tellurium as said elemental chalcogen and at least one other chalcogen selected from the group consisting of sulfur and selenium.

3. The method of claim 1 wherein said first and second temperatures are within the range of 825° C. to 1025° C.

4. The method of claim 1 wherein the temperature of said growing crystal is below said second temperature during crystal growth by approximately 2 to 10 centigrade degrees.

5. The method of claim 2 wherein the quantity of elemental tellurium in said envelope is a quantity sufficient to produce upon complete vaporization thereof a partial pressure of approximately 5×10^{-2} to 5×10^{-1} atmospheres of tellurium vapors therein.

6. The method of claim 2 wherein the pseudo-binary chalcogenide compound is represented by the chemical formula:

$$MSe_xTe_{(1-x)}$$

where M is zinc, cadmium, or a mixture thereof.

7. The method of claim 2 wherein the temperature of said growing crystal during crystal growth is approximately 2 to 10 centigrade degrees below said second temperature and the quantity of elemental tellurium within said envelope is sufficient to produce upon complete vaporization thereof a partial pressure of tellurium within said envelope of approximately 5×10^{-2} to 5×10^{-1} atmospheres of tellurium vapor.

8. The method of claim 7 wherein said pseudo-binary compound is represented by the chemical formula

$$ZnSe_xTe_{(1-x)}$$

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