June 16, 1959 L. E. RAVICH 2,890,939

CRYSTAL GROWING PROCEDURES

Filed Feb. 8, 1955 3 Sheets-Sheet 1

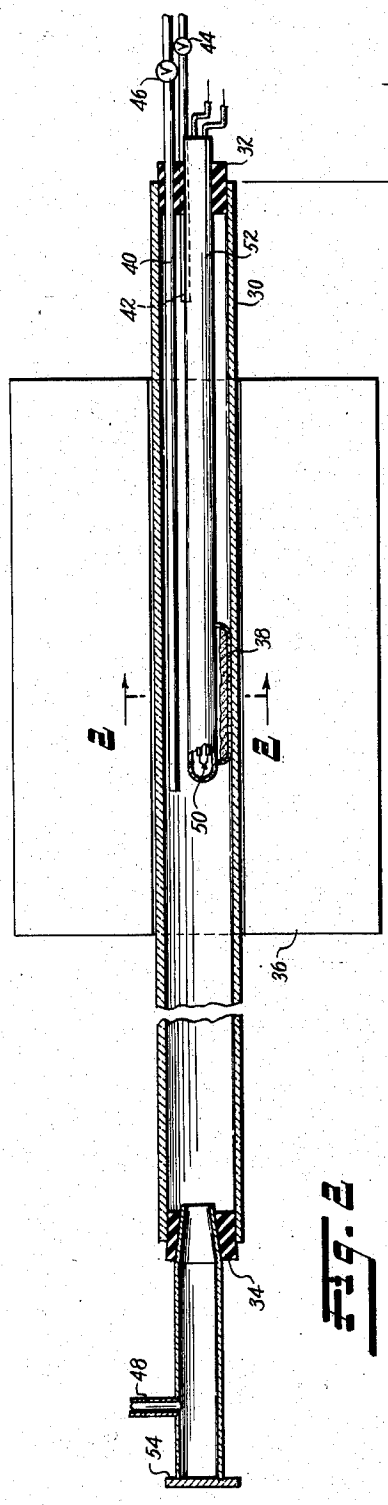


Fig. 1

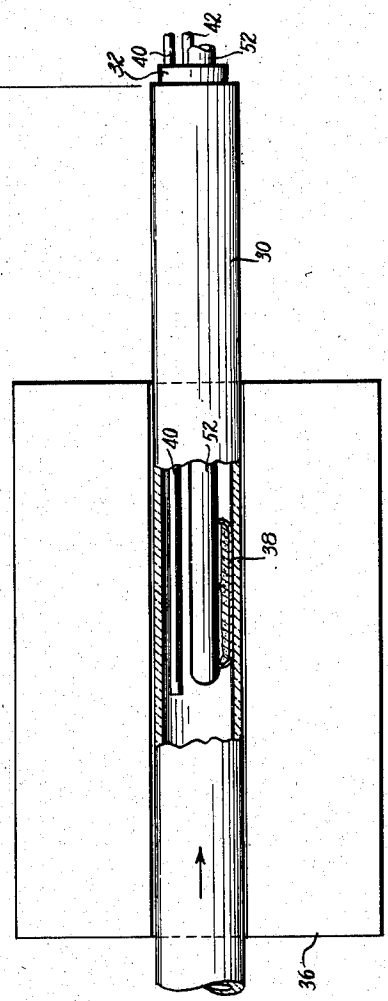


Fig. 3

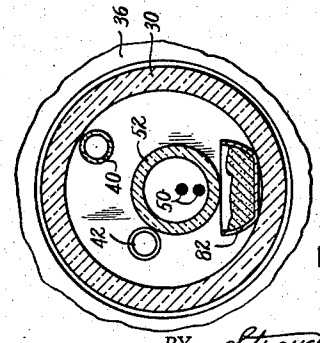


Fig. 2

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CRYSTAL GROWING PROCEDURES

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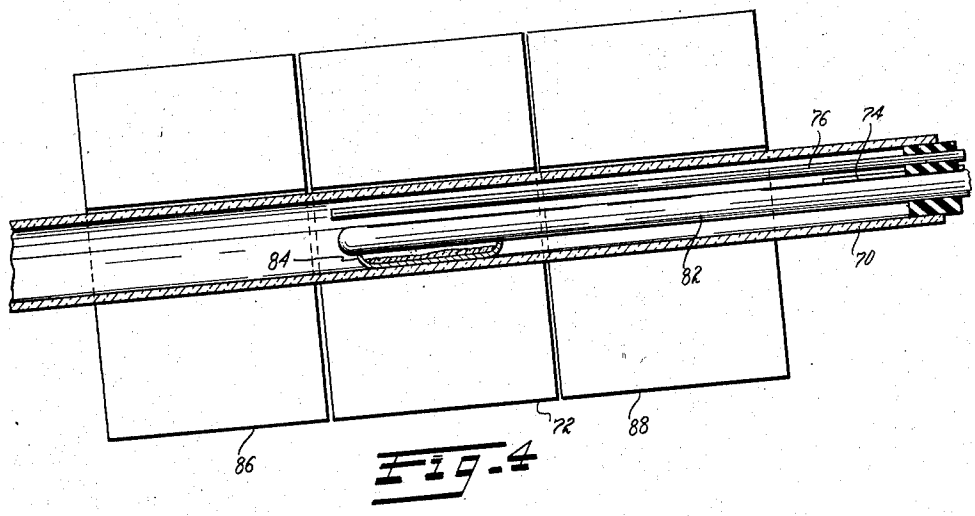


Fig-4

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June 16, 1959 L. E. RAVICH 2,890,939

CRYSTAL GROWING PROCEDURES

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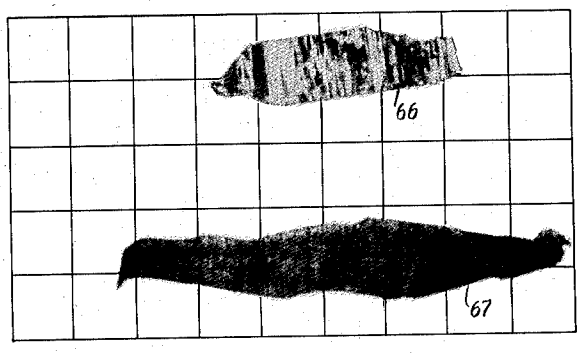


Fig. 6

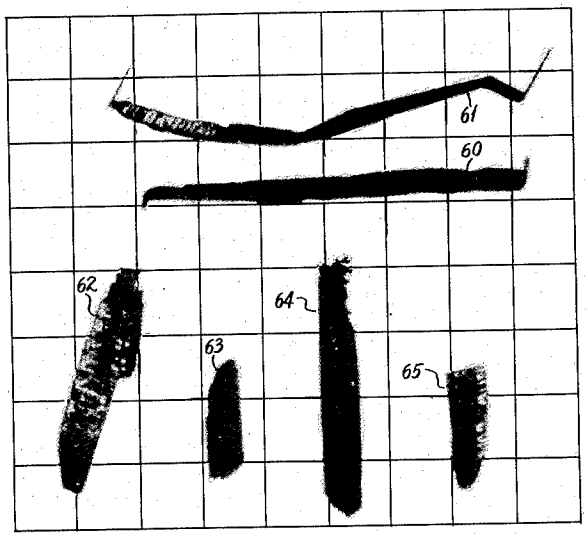


Fig. 5

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United States Patent Office 2,890,939 Patented June 16, 1959

2,890,939

CRYSTAL GROWING PROCEDURES

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Application February 8, 1955, Serial No. 486,927

13 Claims. (Cl. 23—294)

This invention relates primarily to new and improved methods for growing crystals of semiconductor materials and more particularly to improved techniques for quantity production of cadmium sulfide and like metal sulfide crystals of desired size and degree of purity and having predetermined response characteristics.

This application is a continuation-in-part of my copending application Serial No. 329,973, filed February 7, 1953.

The semiconductor materials to which this and the above said copending application relate are those binary metal compounds, as distinguished from elements, which react in a predetermined pattern when subjected to one or more external stimuli as for example radiation sensitive elements such as photo-resistive, photo-generative or photo-capacitive, and also to semiconductor components which respond in a predetermined manner to the application of a constant and/or variable electrical potential or which exhibit the transistor effect.

The sulfides of cadmium, lead and zinc are the most desirable of these semiconductor compounds because of their high sensitivity and other desirable response characteristics and also their versatility of application, but prior to the present invention the use of these metal sulfides has been severely limited by the difficulty and high cost of obtaining them in crystal form, particularly as mono-crystals of relatively large size and desired purity. The present invention relates to new and improved methods for producing semiconductor crystals of these and similar compounds consistently, economically and in good quantity per production run. While these novel crystal growing procedures will hereinafter be described in detail only as to cadmium sulfide, it is to be understood that in certain aspects they are equally applicable to growth of crystals of other binary metal compounds particularly the other metal sulfides mentioned.

Heretofore it has been customary in efforts to produce cadmium sulfide crystals to use cadmium metal as the source of cadmium, and generally such prior art methods have succeeded in producing only impure cadmium sulfide crystals containing metallic cadmium as an impurity. The presence of this impurity can readily be recognized by the greenish-yellow color, lack of transparency, and poor photo and electrical characteristics of crystals produced by these prior methods. In addition to this lack of purity, it has been impossible to produce consistently crystals of sufficient size for use as electrical circuit components, the usual cadmium sulphide crystal produced by such prior art methods being in the form of a long but very thin needle. A description of one such method heretofore used in an effort to produce cadmium sulphide crystals will be found in Physical Review, volume 52, No. 7 of October 1, 1947, at page 594 et seq., in an article by Rudolf Frerichs entitled "The Photo Conductivity of 'Incomplete Phosphors'."

It has also been proposed to utilize finely powdered crystalline cadmium sulfide as the starting substance, this material being placed in a growing tube and furnace generally similar to that of Frerichs and the furnace temperature slowly raised to and then held at approximately 900° C., meanwhile passing a constant flow of hydrogen and hydrogen sulfide gases over the cadmium sulfide powder. This crystal growing method is said to produce crystals in the form of grooved transparent yellow leaflets.

Generally, however, crystal production by the method just described is very erratic and many production runs yield few or no crystals. Other runs yield only impure crystals having unsatisfactory response characteristics, and the crystals produced generally are relatively small in size, particularly in thickness.

The crystal growing procedures of the present invention similarly employ powdered cadmium sulfide as the starting material, but differ from the prior growing procedures in being capable of producing crystals of large size and desired purity consistently and in good quantity per production run. In accordance with the invention, each crystal production run is divided into crystal seeding and seed growing phases, the temperature and gas flow conditions maintained within the growing tube being such as to induce seed crystal formation during the first phase and to promote optimum growth of crystals on the thus formed crystal seeds during the second phase. The change in temperature and/or gas flow conditions necessary to the transition between these phases preferably is according to the invention carried out by the means and in the manner more particularly described hereinafter. I have found that certain other factors also are critical to quantity production of satisfactory semiconductor crystals and to disturbance point distribution in the crystals produced, as will later be fully explained herein.

Accordingly, it is the primary object of the invention to provide new and improved methods for quantity production of semiconductor crystals particularly of cadmium sulfide, characterized by large crystal size, desired degree of purity and optimum response characteristics.

More specifically it is an object of the invention to provide new and improved crystal growing procedures and apparatus capable of quantity production of semiconductor compound crystals and incorporating steps and means for initiating seed crystal formation and promoting optimum crystal growth on the seed crystals formed.

It is also an object of the invention to provide novel semiconductor crystal production methods wherein crystal growing conditions are varied during the production run to provide a first phase wherein conditions are such as to induce seed crystal formation and a second phase wherein conditions are modified to promote crystalline growth of the preformed seed crystals.

A further object is the provision of metal sulfide crystal production methods wherein a powder of the metal sulfide is vaporized in a growing tube and condensed upon pre-formed seed crystals maintained at a temperature to permit proper molecular orientation to produce crystalline growth.

It is another object of the present invention to provide semiconductor compounds and methods of producing such semiconductor compounds with which, by control of the disturbance point distribution in the compounds, semiconductor elements having predictable characteristics in response to particular stimuli are readily productible.

Still another object is the provision of novel methods for controlling disturbance point distribution in semiconductor crystals by controlled cooling of the crystals after production.

These and other objects of the present invention will become more fully apparent by reference to the appended

claims as the following detailed description proceeds in reference to the accompanying drawings wherein:

Figure 1 is a diagrammatic illustration of one form of apparatus used in the production of semiconductive mono-crystals in accordance with the present invention;

Figure 2 is a section taken substantially on the line 2—2 of Figure 1;

Figure 3 is a view similar to Figure 1 showing the crystal growing tube shifted a distance *"d"* with respect to the associated furnace for promoting crystal growth in accordance with the crystal growing procedures of the present invention;

Figure 4 is a diagrammatic illustration of an alternative form of apparatus used in the production of semiconductive mono-crystals; and

Figures 5 and 6 are reproductions of photographs illustrating various sizes, shapes and internal structural formations of cadmium sulfide crystals which have been produced in accordance with the methods of the present invention.

With continued reference to the drawings, wherein like reference numerals are used throughout to designate like elements, Figures 1 and 2 show an illustrative form of apparatus which may be used in accordance with the invention for growing metal sulfide crystals, such as those of cadmium sulfide or zinc sulfide. As shown, the apparatus comprises a combustion tube **30** preferably of fused quartz or the like which is sealed at both ends as by rubber stoppers **32** and **34** or equivalent means and which slidably extends through the center of a cylindrical electric furnace designated by reference numeral **36** which may be of conventional type capable of producing temperatures preferably well above 900 degrees centigrade. Within the quartz tube **30** at approximately the center of furnace **36** is provided an elongated crucible or boat **38** formed of a suitable refractory material such as sellmanite or alundum. Through the right hand or inlet end of the quartz tube **30** extend suitable gas conduits **40** and **42** which may likewise be formed of quartz. Conduit **42** terminates within and is open into the quartz tube **30** adjacent the inlet end through which it extends and is connected externally of quartz tube **30** to a suitable source of dry hydrogen gas preferably of high chemical purity through a suitable flow control element **44** which can produce either a continuous or pulsating gas flow and which may take the form of any suitably constructed adjustable pressure responsive valve. The conduit **40** is connected at its inlet end to a suitable source (not shown) of dry hydrogen sulfide gas, also preferably of high chemical purity, through a similar control element **46**. The conduit **40** extends into quartz tube **30** to a point adjacent the end of the elongated crucible **38** as illustrated. A suitable exhaust conduit **48** is provided at the opposite or outlet end of the quartz tube **30**, and a thermocouple **50** may be provided within a central quartz thermocouple tube **52** for determining the temperature at the vaporizing zone over the boat **38**. A transparent window **54** of quartz or the like may be provided in the outlet end of the combustion tube for observation of the action within the tube.

The absolute sizes of the various components just described may vary between wide limits depending on the sizes and quantity of crystals desired to be produced in the apparatus. I have found, however, that the relative sizes and placement of the components is a critical factor in attaining optimum crystal growth. For best results it generally is desirable that the cadmium sulfide containing crucible **38** be positioned substantially centrally of furnace **36**; the hydrogen supply conduit **42** should have its outlet end located a substantial distance from the crucible so as to permit the hydrogen flow therefrom to stabilize and become uniform throughout the cross-section of the growing tube before passing over the crucible; the hydrogen sulfide supply conduit **40** should extend to and preferably slightly beyond the downstream end of the crucible; and the thermocouple tube if used preferably is placed directly over and touching the crucible. Relative placement of components varies in each furnace depending on the dimensions of the different components, heating characteristics of the furnace, the presence or absence of a thermocouple tube, and other factors; hence the dimensions and placement of these growing apparatus components can not be set forth with mathematical exactitude though they may readily be determined for apparatus of given size by routine tests therewith conducted in light of the guiding principles disclosed herein.

Prior to commencement of the crystal growing operation, the crucible **38** is filled with cadmium sulfide preferably in the form of a finely divided powder which should be chemically pure if chemically pure crystals are desired to be produced. While for certain of the above enumerated applications of cadmium sulfide and like semiconductor crystals it is desirable that the semiconductor compound include impurities for modifying response characteristics by creating disturbance points in the crystals, it is in general preferred that the starting materials be substantially chemically pure. Then, if disturbance point creating impurities are desired in the end product, they may subsequently be added to the substantially pure starting material in measured and controlled quantity thus providing reproducible performance characteristics in the finished product.

Cadmium sulfide sublimes at a temperature of approximately 980° in nitrogen or predominantly nitrogen atmosphere but the vapor pressure of the system and thus the sublimation temperature of the cadmium sulfide will be lowered if the sulfide is heated in an atmosphere of hydrogen. If in the apparatus of Figures 1 and 2, cadmium sulfide powder is placed in crucible **38** and the crucible positioned in combustion tube **30** in proper relationship to the hydrogen gas supply conduit **42**, the flow of hydrogen over the crucible will cause the cadmium sulfide contained therein to sublime at temperatures of about 600 to 700° C. depending on rates of gas flow, pressures etc. The sublimed vapors will then be carried along by the hydrogen gas flow to a point in combustion tube **30** just downstream of the inner end of hydrogen sulfide gas supply conduit **40**, where, in the presence of the hydrogen sulfide supplied through that conduit, they condense and immediately precipitate in crystalline form on the walls of and within tube **30** in the growing area downstream of the crucible.

It is believed that in this crystal growth process an equilibrium exists between the hydrogen and entrained cadmium sulfide vapors flowing downstream from the crucible, and the introduction of hydrogen sulfide disturbs this equilibrium and causes precipitation of cadmium sulfide. Regardless of the validity of this explanation, however, it is fact that when the cadmium sulfide vapors pass from the sublimation zones, over crucible **38**, to the zone in which the hydrogen sulfide gas flow enters the combustion tube, they will under proper conditions as herein specified precipitate and deposit in tube **30** first as a tiny "seed," then as a needle crystal and, finally, as large plate-like crystals of substantially pure cadmium sulfide.

The sublimation of the cadmium sulfide powder should take place under conditions such that any dissocation of the sulfide is only transitory and the cadmium sulfide does not decompose to form metallic cadmium and free sulphur either in the crucible in which sublimation occurs or during condensation of the vapors onto the crystals being grown. Otherwise metallic cadmium may be present in quantity as an impurity in the crystals produced and this may adversely affect crystal response characteristics.

In accordance with the invention, the crystal production cycle is divided into two phases, a seed forming

phase in which tiny seed crystals of cadmium sulfide are formed, and a crystal growth phase in which cadmium sulfide vapors precipitate onto the preformed seed crystals in proper molecular orientation for optimum crystal growth. These phases may partially overlap with both seeding and crystal growth occurring in each or both phases, it being only necessary that during the early part of the production run conditions conducive to seed crystal formation be established and that after sufficient seed crystals have formed conditions be changed so as to induce maximum growth and yield of crystals.

I have found that one method of assuring these results involves first heating the furnace rapidly (up to approximately 15 minutes) to a point at which the temperature over the crucible **38** is approximately 925° C. and then rapidly cooling it (within approximately 15 minutes or less) to 600° C., whereupon seed crystals will form in tube **30** in substantial quantity. The temperature is next gradually raised from 600° C. to approximately 900° C. and large flat crystals then will grow on the seeds previously formed. The longer the furnace is held at this last temperature, the larger will be the crystal formations produced.

I have also found that seed crystals can be produced with a uniform temperature rise, by pulsing the flow either of hydrogen or hydrogen sulfide which disturbs equilibrium conditions within the growing tube and thus promotes formation of seed crystals.

An alternative and preferred method initiating and maintaining crystal growth utilizes the apparatus of Figures 1 and 2 and involves a shift of the combustion tube within the furnace from the position shown in Figure 1 to that shown in Figure 3, the tube being shifted approximately through distance "*d*" (Figures 1 and 3) during the crystal growing procedure in order to promote seed crystal formation and obtain optimum crystal growth on the seed crystals formed.

In carrying out this preferred method, the crucible **38** is charged with cadmium sulfide powder and placed in growing tube **30** in approximately the position shown in Figure 1, the growing tube then being inserted in furnace **36** into position also as shown in Figure 1, with a portion of the inlet end of the tube extending outwardly of the furnace and with the crucible located adjacent the center or slightly toward the outlet end (left-hand end in Figure 1) of the furnace. Hydrogen and hydrogen sulfide gas flows may then be established, in quantity dependent on the size of the growing tube, the sizes and placement of other components of the apparatus, furnace temperature distribution and other factors. In general, however, the initial rate of flow of hydrogen sulfide should be substantially greater than that of the hydrogen. For example, in one embodiment of the apparatus utilizing a growing tube having 1½ inch inside diameter, good results were obtained with initial hydrogen flow at approximately 260 cc. per minute and hydrogen sulfide flow at approximately 850 cc. per minute.

Furnace **36** may be heated as desired up to a temperature of about 650° C., at which time the rate of heating preferably is reduced and furnace temperature more slowly raised to and then held at approximately the 900° C. temperature which I have found to produce optimum crystal growth. The slower heating rate (10° C. per minute, for example) utilized between the 650° C. and 900° C. temperatures specified is preferred because some seed crystal formation occurs between these temperatures and it will be found that more seeds form when the temperature increase is made relatively slow.

A short time, as for example about two minutes, after the furnace and growing tube temperatures have reached 900° C. the hydrogen flow preferably is substantially increased, and the growing tube then shifted a short distance "*d*" (Figures 1 and 3) within the furnace to be in approximately the position shown in Figure 3. The increased hydrogen flow is effective to correspondingly increase the rate of sublimation of the cadmium sulfide, thus accelerating the rate of crystal growth. The subsequent shift of the growing tube within the furnace effects a redistribution of temperature within the growing tube, the portion of the tube in which is located the cadmium sulfide-containing crucible now being positioned in a somewhat cooler zone of the furnace and the portion of the tube in which crystal growth occurs being in a hotter zone of the furnace. This change in temperature distribution has several desirable results, among which are an increase in temperature in the crystal growing zone, just downstream of the crucible, to the optimum temperature for crystal growth, and a decrease in temperature at the crucible itself which limits the increase in sublimation rate caused by the increase in hydrogen flow so as not to become excessive. Being rather sudden changes in growing conditions, the gas flow increase and temperature redistribution also tend to initiate and promote further seed crystal formation.

Thus, there are two phases to the growing procedure just described, the first phase being the seed forming phase and the second being the crystal growing phase, the gas flow rates and temperature distribution within the growing tube differing in the two phases as specified. In the first phase, the sublimation zone (the portion of the growing tube in which is located the crucible containing the material to be sublimed) is positioned in the central, highest temperature region of the furnace, the crystal growing zone downstream of the crucible is positioned in a relatively cooler region of the furnace, and the hydrogen flow rate is relatively low, thus establishing optimum conditions for seed crystal formation. During the second phase, the hydrogen gas flow rate is increased to accelerate sublimation of the crystal growing material and crystal growth, and the temperature distribution in the growing tube is modified so as to promote sublimation and precipitation of cadmium sulfide in proper molecular orientation for crystalline growth and to inhibit concurrent precipitation of metallic cadmium as an impurity in the crystals being grown. The change in growing conditions attendant on the transition between these different phases of the growing procedure also is of advantage for its tendency to cause formation of seed crystals, adding to those produced prior to the change.

In this growing procedure, as in the procedure first described, the relative sizes and placement of components, zone temperatures, and gas rates of flow and velocities in the combustion tube all are important to successful production of substantially pure crystals of good size and in quantity, and therefore should be properly correlated in the particular growing apparatus to be utilized.

I have observed that the crystals during their formation by the processes just described first grow rapidly to an elongated form and, after reaching almost full length, grow slowly in a direction normal to that of initial growth along the entire crystal length to form a plate-like structure. As the plate-like structure develops there will be some increase in thickness of the plate and a generally slight increase in length from the initial length of the crystal formed.

So far as is presently determined, the only limitations on the size of cadmium sulfide crystal mono-crystalline plates which can be formed by the processes of this invention are those imposed by the size of the combustion tube in which they are grown and the quality of armorphous cadmium sulfide which can be placed in the tube. These methods have consistently produced crystals of the size illustrated in Figures 5 and 6 and larger, from approximately five grams of cadmium sulfide powder as the starting charge. These crystals are shown in Figures 5 and 6 on a grid network in which each of the squares has sides five millimeters in length.

I have found that the sensitivity to radiation of the met-

al sulfide crystals produced by the methods of this invention may vary in accordance with the manner in which the crystals are cooled. If the cadmium sulfide crystals while still in the combustion tube are cooled slowly (up to 48 hours) a practically transparent crystal results which has a minimum number of disturbance points and is highly sensitive to radiation. The crystal designated **60** and the right hand portion of crystal **61** (both shown in Figure 5) are of such transparent structural formation. If the cadmium sulfide crystal is cooled rapidly (in about 15 minutes or less), many disturbance point creating strains and other imperfections are formed in the crystal in the manner illustrated by crystals **62**, **63**, **64**, and **65** in Figure 15 and by crystals **66** and **67** in Figure 6. Crystals of maximum imperfection density exhibit a relatively low response to stimulation by radiation but exhibit rectifier characteristics, upon stimulation by an applied electrical potential, whereby they may be utilized as transistors of either the point contact or junction type. It will be noted that the upper ends of crystals **62** and **64** have many smaller crystals grown upon the main mono-crystal. This growth may result if the temperature of the main mono-crystal drops below the temperature for proper molecular orientation during the crystal forming process. Such growth structures have various desirable characteristics as, for example, photo-voltaic effects and high time constants for memory effects.

A preferred form of the apparatus for producing cadmium sulfide crystals in accordance with the methods of the present invention is illustrated in Figure 4. As in the apparatus illustrated in Figures 1–3, a quartz combustion tube **70** is slidably mounted in and extends through an electric furnace **72** and is provided through its inlet end with gas conduits **74** and **76** for introducing hydrogen and hydrogen sulfide, respectively, into the quartz tube **70**. Conduit **74** is connected through a suitable control element, which may be similar to the valve **44** shown in Figure 1, to a suitable source (not shown) of dry pure hydrogen gas, and conduit **76** is connected through a similar control element to a suitable source (not shown) of dry pure hydrogen sulfide gas. A quartz or other thermocouple tube **82** extends centrally through combustion tube **70** over the elongated crucible or boat **84** which contains cadmium sulfide in powder form. The thermocouple tube **82** provides a means for ascertaining the temperature of the furnace immediately over the crucible **84** while preventing corrosion or contamination of the thermocouple contained in the tube.

The apparatus of Figure 4 differs from that of Figures 1–3 primarily in that it includes two additional independently controllable electric furnaces, **86** and **88**, one being located on either side of crucible **84** in the sublimation zone of quartz tube **70**. If desired, a thermocouple may be provided within the crystal forming zone downstream of crucible **84** in addition or in preference to that directly over the crucible, to permit ready and more accurate control of the temperature at the growing zone. It also is possible to substitute furnace temperature thermocouples for those mounted internally of the growing tube, or to use both types if desired.

As has been indicated previously, the temperatures of both the vaporization and crystal forming zones of the growing tube during crystal growth are extremely important. In the apparatus of Figure 4 it is possible to control the temperature of the crystal forming zone independently of that at crucible **84**; hence the temperature of the center furnace **72** may be raised to any temperature necessary or desired for vaporizing the cadmium sulfide in crucible **84**, independently of the temperature maintained at the growing zone downstream of the crucible.

The temperature of furnace **86**, which encloses the crystal growing zone of combustion tube **70**, preferably is first raised more slowly than furnace **72** and only to a temperature at which the vaporized cadmium sulfide can readily condense on the walls of tube **70** to form seed crystals thereon. After seed crystals have formed on the walls of the tube **70**, the temperature of furnace **86** may then be further raised to the temperature at which the cadmium sulfide vapors precipitate onto the pre-formed seed crystals to produce crystalline growth in mono-crystalline form, which temperature may as noted above be approximately 900° C.

The furnace **88** adjacent the inlet end of the growing tube preferably is controlled to provide a smooth temperature gradient between the sublimation zone of the growing tube and the inlet end thereof, and to heat the hydrogen and hydrogen sulfide gases fed into the tube to the proper temperatures for optimum crystal growth.

As is apparent from the foregoing, the three independently controllable furnaces shown in Figure 4 make possible a modified crystal growing procedure which in many respects is equivalent to the preferred method described above in reference to Figure 3, wherein the combustion tube is shifted to effect a temperature redistribution. With the apparatus of Figure 4, however, no physical movement of the tube during the growing process is required, the desired temperature redistribution being instead effected by proper re-adjustment of the temperature of the several furnaces. This re-adjustment may if desired be accompanied by an increase in hydrogen gas flow rate in the manner hereinbefore described. Additional advantages of the plural furnace arrangement are the more accurate temperature control obtainable therewith and the wider temperature differentials between different zones of the growing tube which may be established and maintained where necessary or desirable to initiate seed growth or to permit ready sublimation of the cadmium sulfide powders and produce condensation thereof upon the crystal seeds while maintained at the proper temperature for best crystal growth.

By the provision of additional independently controllable furnaces or heating elements, such as at **86** and **88**, it also becomes possible to provide a much larger crystal forming zone due to the ability to maintain greater portions of the length of tube **70** at temperatures appropriate for seed crystal formation and for monocrystalline growth, respectively. In addition, it is possible in the apparatus of Figure 4 to more readily control the rate of cooling of the crystals after complete growth has been attained.

It is to be understood that a single furnace having plural independently controlled heating elements or other means permitting adjustment of the temperature gradient along the length of the furnace, may if desired be substituted for the three separate furnaces illustrated.

From the foregoing detailed description it is apparent that I have provided certain new and useful improvements in processes for quantity production of crystals of cadmium sulfide and other metal sulfide semiconductor compounds, the improved processes being characterized by good crystal yield per production run and by large crystal size and optimum response characteristics in the crystals produced.

The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The present embodiments are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

I claim:

1. The method of producing cadmium sulfide crystals which comprises the steps of providing a supply of cadmium sulfide in powder form in a growing chamber having a first portion and a second portion, effecting vaporization of the cadmium sulfide in the first portion of said chamber and condensation of the resulting vapors in

the second portion of said chamber initially under conditions effective to induce formation of seed crystals, there being a first temperature difference between the temperature of said first and said second portions during the formation of said seed crystals, and continuing the step of vaporization under changed conditions wherein said temperature difference is reduced to promote crystalline growth of the pre-formed seed crystals, and cooling the crystals so formed to ambient temperature.

2. The method defined in claim 1 wherein the reduction in temperature difference between said growing chamber portions is accompanied by a change in rate of vaporization of the cadmium sulfide powder.

3. The method defined in claim 1 wherein said crystal cooling is effected slowly to produce a crystal having a minimum number of disturbance points therein.

4. The method defined in claim 1 wherein said crystal cooling is effected rapidly to produce a crystal having a maximum number of disturbance points therein.

5. The method of producing cadmium sulfide crystals which comprises the steps of providing a supply of cadmium sulfide in powder form in a growing chamber, passing hydrogen gas through the chamber and over the cadmium sulfide contained therein to substantially lower the vaporization temperature thereof, heating the cadmium sulfide contained in said growing chamber to vaporize into and be entrained by the hydrogen flow, inducing precipitation of the entrained cadmium sulfide vapors, initially maintaining a temperature gradient between the portion of the growing chamber in which the cadmium sulfide is vaporized and that in which the resultant vapors are condensed effective to promote seed crystal formation, and thereafter modifying said temperature gradient to promote crystal growth on the seed crystals thus formed.

6. The method defined in claim 5 wherein hydrogen sulfide is introduced into the cadmium sulfide entraining flow of hydrogen within the growing chamber to induce precipitation of the cadmium sulfide therefrom.

7. The method defined in claim 5 wherein the growing chamber is provided with heating means and the variation of chamber temperature is effected by movement of the heating means with respect to the chamber.

8. The method defined in claim 5 wherein the growing chamber is provided with a plurality of spaced, independently controllable heating means and the variation of chamber temperature is effected by individual adjustment of the several heating means.

9. The method defined in claim 5 including the step of producing a variation in the rate of hydrogen flow through the growing chamber adjunctively to the variation of chamber temperature.

10. A method of growing cadmium sulfide crystals in a crystal growing chamber provided with heating means and having hydrogen gas introduction means, hydrogen sulfide gas introduction means and an exhaust opening spaced serially along the length of the chamber; comprising the steps of providing a supply of cadmium sulfide in powder form and placing the same in said growing chamber between said hydrogen and hydrogen sulfide gas introduction means, adjusting said hydrogen gas introduction means to provide a flow of hydrogen over the cadmium sulfide effective to substantially depress the vaporization temperature thereof, operating said heating means to raise the temperature of the cadmium sulfide at least to the thus depressed vaporization temperature thereof to cause the cadmium sulfide to vaporize into the hydrogen flow thereover, adjusting said hydrogen sulfide gas introduction means to provide a flow of that gas into the cadmium sulfide bearing hydrogen to induce condensation of the cadmium sulfide vapors from the hydrogen in proper molecular orientation for crystalline growth, initially maintaining a temperature gradient between the portion of the growing chamber in which the cadmium sulfide is vaporized and that in which the resultant vapors are condensed effective to promote seed crystal formation, and thereafter modifying said temperature gradient to promote crystalline growth on the seed crystals thus formed.

11. The method defined in claim 10 wherein said temperature gradient is modified by physical movement of the growing chamber with respect to its heating means.

12. The method defined in claim 10 wherein the heating means includes a plurality of independently controllable heating elements and said temperature gradient is modified by individual adjustment of the heating elements.

13. The method defined in claim 10 including the step of increasing the rate of flow of hydrogen over the cadmium sulfide when the temperature of the cadmium sulfide has risen above the vaporization temperature thereof.

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