Feb. 11, 1964 H. J. GOULD 3,121,062

VAPOR PHASE CRYSTALLIZATION

Filed June 22, 1961

FIG. 1.

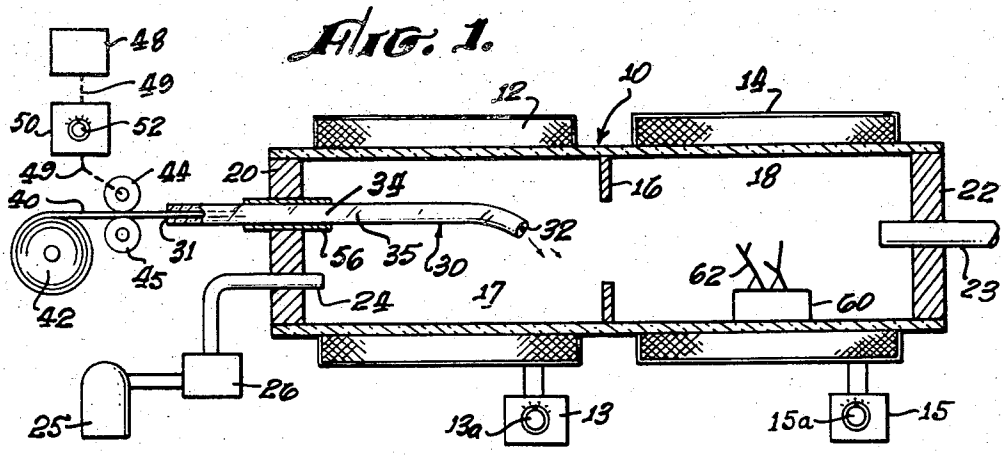



FIG. 2.

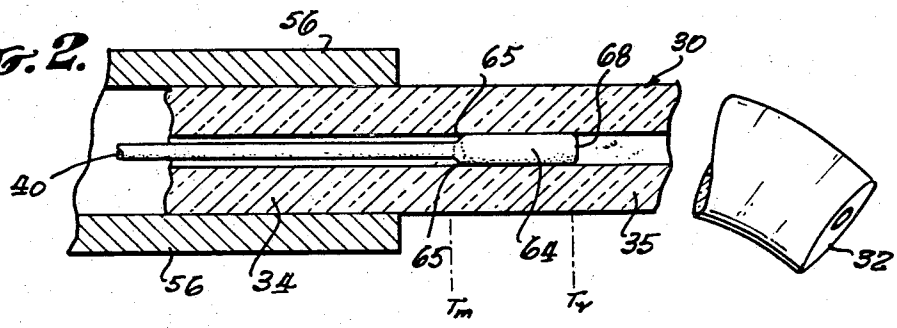
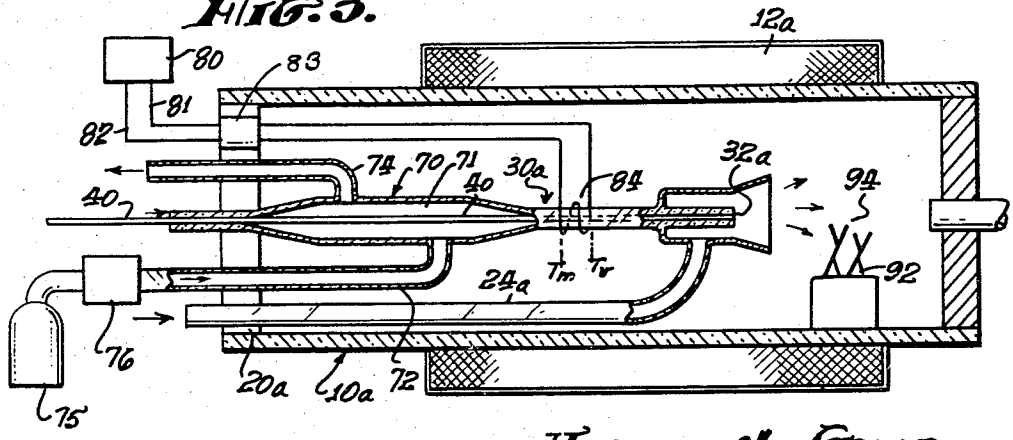



FIG. 3.




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# VAPOR PHASE CRYSTALLIZATION

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This invention has to do with the crystallization from the vapor phase of crystals at least one component of which is a metal that is solid at normal temperature.

The invention has to do, more particularly, with improved methods and apparatus for supplying to a furnace chamber the vapor of a metallic component that is solid at normal temperature.

The invention is particularly useful in, but is not limited to, the production of semiconductive crystals, such, for example, as cadmium and zinc sulphide, selenide and telluride and mixtures of such components. It is well known that crystals of that type can be produced in good purity by vapor phase crystallization.

In producing such illustrative crystals the non-metallic component is ordinarily supplied to the furnace as a continuous stream of gas, typically as hydrogen sulphide, selenide or telluride. The rate of supply of such a gaseous component is accurately and conveniently controllable by known methods.

The metallic component is ordinarily supplied by inserting in the furnace in the gas stream a boat containing the metal in solid or liquid form. The metal then evaporates into the gas stream at a rate that is roughly controllable by variation of such factors as the temperature, the rate of gas flow and the area of the exposed metal surface.

Such control, however, is less accurate than is often desirable, and is unsatisfactory for many other reasons. Even rough control of the vaporizing temperature usually requires a special furnace zone for that purpose. The rate of gas flow that is most suitable for metal vaporization may be undesirable for other reasons. And the area of metal surface usually decreases in an uncontrollable way as the initial charge is exhausted. Moreover, the rate of evaporation from a given surface area is very sensitive to contamination of the surface, which typically increases as the metal charge is consumed.

The present invention avoids all of those difficulties in a remarkably economical and convenient manner. In accordance with one aspect of the invention, the metallic component is supplied in the form of a fine wire, and is fed to the furnace at a definite velocity. The metal vaporizes continuously as it reaches the point of vaporizing temperature. The rate of metal vapor supply to the furnace chamber is then conveniently and accurately controllable by mechanical variation of the feed velocity. The described method has the further great advantage that under equilibrium conditions of operation the rate of vapor supply is essentially or completely independent of virtually all other variable factors. Hence those factors may be adjusted arbitrarily as required to meet other conditions.

In accordance with a further aspect of the invention, the metal wire is fed to the furnace chamber through a capillary passage formed of suitable inert material, such as quartz, for example. The passage is so arranged that the advancing metal reaches vaporizing temperature at a point spaced from the exit mouth of the passage. Vaporization then occurs within the capillary passage, and the metal leaves the passage mouth as a continuous and uniform stream of vapor. A further advantage of that structure is that, by suitable form and placement of the passage, the metal vapor can be delivered accurately to any desired point of the furnace chamber.

A further aspect of the invention provides means for surface cleaning of the metal wire immediately prior to



melting and vaporization. That may be accomplished by passing the wire through a reducing chamber which is continuously washed by a reducing gas, such as hydrogen, for example. The reducing chamber is preferably maintained at an elevated temperature, which may be only slightly less than the melting point of the metal.

A full understanding of the invention, and of its further objects and advantages, will be had from the following description of certain illustrative manners in which it may be carried out, of which description the accompanying drawings form a part. The particulars of that description are intended only as illustration, and not as a limitation upon the scope of the invention, which is defined in the appended claims.

In the drawings:

FIG. 1 is a schematic drawing of illustrative apparatus in accordance with the invention, including a schematic axial section of a typical furnace;

FIG. 2 is a fragmentary detail of FIG. 1 at enlarged scale;

FIG. 3 is a fragmentary section representing a modification.

In the drawings an illustrative furnace tube is represented at **10**, typically constructed of fused quartz. Electrical heating coils are represented at **12** and **14**, with respective power sources **13** and **15**. An apertured baffle **16** partially divides the furnace chamber into two zones **17** and **18**, which may be maintained at different temperatures. Temperature control apparatus is typically incorporated in the power sources, permitting the temperatures of the respective furnace zones to be separately controlled, as by adjustment of calibrated dials indicated at **13***a* and **15***a*. Both ends of furnace tube **10** are typically closed by apertured plugs, shown at **20** and **22**.

For growing a typical crystal derived from one gaseous component and one metallic component, the gaseous component is introduced into zone **17** of the furnace tube via an entrance tube **24**, which is typically of quartz and mounted in a bore in plug **20**. The desired gas such, for example, as hydrogen sulphide, hydrogen selenide or hydrogen telluride may be supplied to tube **24** from a suitable tank or generator **25** via a flow control device **26**, which may be of conventional type. Means of known type may also be provided for washing furnace tube **10** with any desired inert or reagent gas prior to each crystallizing operation. An outlet tube **23** is provided in end plug **22**, leading typically from zone **18** to the atmosphere, or to suitable disposal apparatus. If the furnace is to be operated at reduced pressure, for example, outlet tube **23** may be connected to a vacuum pump.

In accordance with one aspect of the present invention, a capillary tube **30**, preferably of fused quartz, is mounted, as in a bore in plug **20**, with its inlet end **31** outside of the furnace and its outlet end **32** within the furnace at any desired point. As illustratively shown, tube outlet **32** is in furnace zone **17** in the general vicinity of baffle **16**. However, the tube outlet may be placed at substantially any position and with any direction of delivery that may be desired.

A metal wire is represented at **40**, consisting essentially of the metal component required as vapor for reaction and crystallization with the gas from tube **24**. As an illustration, the wire may be formed primarily of cadmium or zinc. Wire **40** is taken typically from a supply spool **42** and is fed between two feed rolls **44** and **45** into inlet end **31** of capillary **30**. The feed rolls are preferably made of a slightly yielding and chemically inert material such, for example, as polymerized tetrafluoroethylene, which is available commercially under the trade name Teflon. The rolls are driven from a suitable motor and speed reduction gear, indicated schematically at **48**, via

a driving connection 49. Connection 49 preferably includes a continuously variable speed control, represented schematically at 50, with speed adjusting dial 52. From the known wire diameter and density, a suitable feed velocity can then be obtained conveniently, to supply metal to the furnace at any desired rate. In practical crystallizing processes for making semiconductors of the type described, suitable feed rates are typically obtainable with wire sizes in the range from 30 gauge to 20 gauge and with feed velocities from about 1 mm. to about 10 mm. per minute.

With the typical arrangement of FIG. 1, the metal vapor issues from tube 30 at 32 into furnace zone 17, which contains essentially an atmosphere of gas from tube 24. That gas is maintained above the vaporizing temperature of the metal, so that vaporization occurs typically well within tube 30. The gas and vapor mixture passes through baffle 16 into furnace zone 18, which is maintained at a suitable crystallizing temperature. A suitable base for crystal formation and growth may be provided in chamber 18 and is indicated schematically at 60 with growing crystals represented at 62. The residual gas and vapor leave via tube 23.

In accordance with a further aspect of the invention, the advancing wire 40 is caused to pass through a relatively steep temperature gradient which extends through the temperatures of melting and boiling of the wire. In FIG. 1, for example, a sleeve 56 of a metal having a high temperature conductivity closely encloses tube 30 where it passes through the furnace wall. The outer portion of sleeve 56 is cooled by exposure to the atmosphere outside the furnace. Additional cooling means of conventional type, not explicitly shown, may be provided if desired. Tube 30 is thus subject to a sharp temperature gradient between the portion indicated at 34 just within sleeve 56, which is cooled by conduction along the sleeve, and the portion 35 just beyond the sleeve, which is exposed to substantially the full heat of furnace chamber 17. That gradient is preferably much steeper than the temperature gradient existing in the furnace chamber itself directly adjacent the tube.

The portion of tube 30 at the high temperature gradient is shown at enlarged scale in FIG. 2. As wire 40 advances to the right as seen in the figures, it reaches melting temperature at a point indicated typically at $T_m$, forming a drop of molten metal 64. As fresh liquid is formed it is prevented from flowing back to the left by surface tension at the faces 65 and by the gradually advancing wire. The liquid therefore moves to the right, advancing the front face 68 of the drop progressively along the tube to higher temperatures. At some point, denoted $T_v$ in FIG. 2, a vaporizing temperature is reached at which the rate of metal evaporation from surface 68 just equals the rate at which metal arrives at the surface from the left as liquid. Under such equilibrium vaporizing surface 68 remains fixed, and the rate of vaporization corresponds accurately to the rate of feed of solid wire 40.

If some condition, such as furnace temperature, is then changed slightly, vaporizing surface 68 shifts correspondingly to a new equilibrium position. That shift involves a temporary change in rate of vaporization. However, the magnitude of such change is inherently small if the temperature change is gradual; and is further limited by the small sectional area of the capillary bore. Further, the steeper the temperature gradient near surface 68, the smaller the axial movement of that surface to its new equilibrium position. By use of a suitably small capillary, and correspondingly fine wire, and by providing sufficiently steep temperature gradient in the neighborhood of $T_v$, the rate of vaporization may be made essentially independent of other factors of the furnace operation. That operation may therefore be adjusted with great freedom to obtain optimum conditions without disturbing the rate of supply of metal vapor.

Also, variation of the feed rate of wire 40 typically causes a small shift of equilibrium position of surface 68, leading to rapid stabilization of vaporization at the new equilibrium rate. Thus the vapor feed rate is controllable accurately and essentially independently of other operating conditions.

With previous methods of supplying metal vapor, if the metal to be vaporized includes a definite proportion of impurity, whether present accidentally or intentionally, the additive usually melts and evaporates at a different rate from the metal. Such fractionation causes progressive changes in concentration of the impurity, both in the vapor produced and in the remaining melt. The crop of crystals is therefore non-uniform, the initial growth, for example, containing more than average concentration of lower boiling impurities and less than average of higher boiling impurities.

With the vapor supply method of the present invention, that difficulty is virtually eliminated. If an impurity initially evaporates from surface 68 at a lower rate, for example, than is proportional to its concentration, the result is to increase the impurity concentration in the liquid closely adjacent surface 68. The rate of vaporization is thereby progressively increased, until a proportional rate is attained. Once equilibrium is established, the vapor leaving tube 30 contains the same proportion of impurity as the wire entering it. An important point is that equilibrium is established rapidly, due primarily to the small area of surface 68 and to the small volume of liquid adjacent that surface. A steep temperature gradient is also helpful in accelerating this type of equilibrium.

Because of the action just described, the method of the invention is well adapted for growing crystals of uniform composition. On the one hand, with metal of high initial purity, the resulting crystals are correspondingly pure and are not degraded, as is usual with previous methods, by concentration of the impurities in the initial or in the final fractions of the growth.

On the other hand, the present method for the first time permits crystals to be grown from the vapor phase containing an accurately controllable and closely uniform concentration of desired impurities.

As an example, it is well known that the photoconductive properties of such semiconductive crystals as cadmium sulphide depend very sensitively upon the concentration of certain impurities, commonly referred to as doping agents. Many such doping agents are well known, including in particular the elements boron, aluminum, gallium, indium, phosphorus, arsenic, antimony and copper, as well as many others. Such doping agents can be added to cadmium metal in the desired concentrations, which are typically extremely small; but it has not previously been possible to produce metal vapor containing an equal, or even a uniform, concentration. With the present method, the accurately doped and thoroughly mixed cadmium, or other vaporizable metal, is drawn or otherwise formed by conventional procedures into a wire of suitable diameter. When the wire is fed to the furnace as already described, any tendency for the doping agent to segregate at the melting or vaporizing face reaches equilibrium rapidly. Thereafter the vapor leaving tube 30 contains a concentration of doping agent that remains essentially uniform and is accurately equal to the selected concentration that is present in wire 40.

FIG. 3 is illustrative of the wide range of modifications that may be made within the scope of the present invention. Furnace tube 10*a* contains only a single furnace zone, the temperature of which is controlled in conventional manner, as by regulation of power supplied to heating coil 12*a*. The metal wire 40 is fed into the left end of tube 30*a*, typically in the illustrative manner already described in connection with FIG. 1.

Metal purifying apparatus in accordance with the invention is indicated generally at 70. The bore of tube 30*a* is locally enlarged, preferably at a point just within the furnace, to form a chamber 71 through which wire 40

passes. Inlet and outlet tubes **72** and **74** communicate between chamber **70** and the outside of the furnace, typically passing through suitable bores in plug **20***a*. A source of a suitable reactive gas, shown schematically at **75**, is connected to inlet tube **72** via a flow control device **76**, which may be of conventional type. The gas thus supplied to chamber **70** forms an atmosphere surrounding wire **40** and reacts readily with any existing surface contamination of the wire. The particular reactive gas employed in each instance is selected, with due regard for the known chemical characteristics of the wire and the impurities that need to be eliminated. For example, a wire of cadmium typically becomes contaminated with surface traces of cadmium oxide. Such traces can be effectively removed by providing in chamber **70** an atmosphere containing hydrogen at an elevated temperature below the melting point of cadmium. Such temperature is usually readily obtainable by placing chamber **90** in a relatively cool part of the furnace, for example near end wall **20***a* as illustrated. Auxiliary heating or cooling means of conventional type may be provided. The hydrogen gas is effectively inert with respect to cadmium metal, but reduces the cadmium oxide impurity to cadmium metal and water vapor, which is carried off through outlet tube **74** with the gas stream.

FIG. 3 further illustrates provision of means for locally heating tube **30***a* to produce a sharp axial temperature gradient. A source of controlled high frequency alternating current power is indicated schematically at **80**. Power leads **81** and **82** are mounted in a suitable insulating bushing **83** in furnace plug **20***a* for supplying power from source **80** to the induction heating coil **84**. Coil **84** surrounds tube **30***a* at a point which is normally cooler than vaporizing temperature of the metal of wire **40**. It is ordinarily advantageous that such induction heating tends to supply heat directly to the metallic wire **40**, providing accurate control of the resulting temperature gradient in the wire. That gradient is indicated schematically in FIG. 3 by the temperature designations $T_m$ and $T_v$, corresponding generally to the similar designations in FIG. 2. Alternatively, a metal sleeve may be mounted on tube **30***a* within induction coil **84**. Heat is then supplied primarily to the sleeve and by conduction therefrom through tube **30***a* to the wire.

Many other known techniques for supplying and controlling the flow of heat may be employed for producing the desired temperature gradient within the scope of the present invention.

FIG. 3 further illustrates means for delivering the stream of metal vapor from the outlet **32***a* of tube **30***a* directly into the stream of fresh gas from gas inlet tube **24***a*. In the illustrative arrangement shown, tube **24***a* opens into a horn structure **90** which coaxially surrounds the outlet portion of tube **30***a*. The fresh gas and metal vapor are then combined in the horn prior to their exposure to the general atmosphere of the furnace. Suitable surfaces of known type for initiating crystallization may be provided in any desired relation to horn **90**. Such means are represented schematically at **92**, with growing crystals indicated at **94**.

I claim:

1. The method of supplying vapor of a metal at a controlled rate to a furnace chamber for production of a crystal by vapor phase crystallization, said method comprising providing a capillary passage communicating with the chamber, feeding a wire consisting essentially of the metal into the passage toward the chamber at a controlled velocity, and maintaining the chamber at such temperature that the wire is vaporized within the passage.

2. The method of supplying vapor of a metal at a controlled rate to a furnace chamber for production of a crystal by vapor phase crystallization, said method comprising providing a capillary passage that opens into the chamber, maintaining in the passage at a point spaced from said opening a longitudinal temperature gradient that is steeper than the gradient in the chamber adjacent the passage and that embraces the melting temperature and the vaporizing temperature of the metal, and feeding a wire consisting essentially of the metal into the passage toward the chamber at a controlled velocity.

3. The method of supplying vapor of a metal at a controlled rate to a furnace chamber for production of a crystal by vapor phase crystallization, said method comprising providing a passage communicating at one end with the chamber, feeding a wire consisting essentially of the metal into the passage toward the chamber at a controlled velocity, maintaining the passage at such temperature that the wire is vaporized therein adjacent said passage end, and contacting the wire in the passage prior to said vaporization with a gas that is substantially inert with respect to the metal and that chemically reacts with impurities carried by the wire.

4. The method of producing a semiconductive crystal comprising a metallic component and containing a substantially uniform relative concentration of a doping agent, said method comprising providing a solid wire which consists essentially of the metallic component and the doping agent in said relative concentration, feeding the the wire at a controlled velocity into a capillary tube, maintaining a temperature gradient along the tube to vaporize the wire, and crystallizing the resulting vapor to form said semiconductive crystal.

5. The method of producing a semiconductive crystal containing substantially uniformly distributed therein a minor proportion of a doping agent, said method comprising providing a solid wire composed primarily of metal selected from the group consisting of cadmium and zinc and containing said doping agent in a concentration corresponding to said proportion, feeding the wire at controlled velocity into a capillary tube, maintaining a temperature gradient along the tube to vaporize the wire, combining the resulting vapor in substantially constant ratio with gas selected from the group consisting of hydrogen sulphide, hydrogen selenide and hydrogen telluride, and crystallizing said semiconductive crystal from the resulting vapor phase.

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