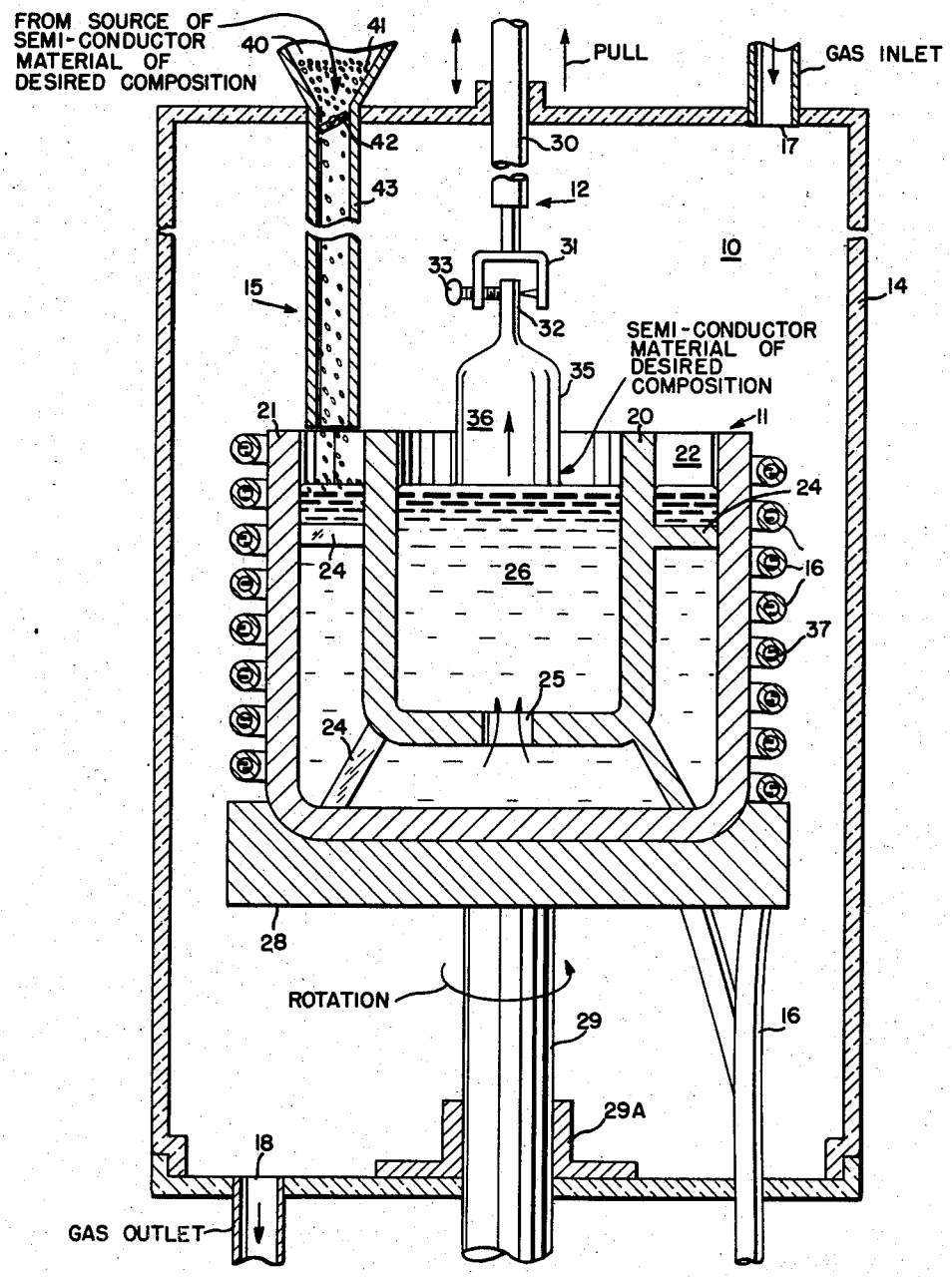
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CRYSTAL GROWING PROCEDURE

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CRYSTAL GROWING PROCEDURE

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The present invention relates to a procedure and apparatus for growing crystals having a substantially constant composition, and more particularly to growing of semi-conductor crystals having substantially constant composition characteristics over an extended portion of their length.

According to procedures presently utilized in semiconductor crystal growing applications, a single-crystal ingot is grown from a melt, the usable portions of the ingot separated from the remainder of the ingot and the usable portion further processed. Generally, the usable portions of the ingot amount to only a relatively small portion of the entire ingot and for this reason the operation is considered rather inefficient at this point.

The usable portions of the crystals may be increased somewhat if the rate of pull is properly programmed. That is, the solid-liquid segregation constant of the mixture may be increased or decreased in accordance with the manner that the crystal is pulled from the melt, for example, if the crystal is pulled more slowly, the segregation constant drops, and the concentration of impurities in the crystal as pulled remains fairly constant over a relatively longer portion of the crystal. This is due to the slow increase in impurity concentration as the crystal pulling progresses. While this method is generally practiced, it is not entirely satisfactory since the size of crystals produced in this manner is limited, and further, the programming rate requires a skilled operators' constant attention over long periods of time. It is well known that in any system wherein the solid and liquid phases are in equilibrium with each other, portions of the impurities present tend to migrate to one phase or the other, and in particular in present day semi-conductor work, the impurities tend to migrate to the liquid phase. Therefore, as a crystal is being withdrawn from a melt the composition of the liquid phase is constantly changing, that is, the liquid portion becomes more heavily contaminated with impurities or in other words contains a relatively higher percentage of impurity members. According to my improved procedure, the composition of the liquid phase is held substantially constant by the addition of new raw material to the melt at a rate substantially equal to the rate of withdrawal of material in the form of the crysalline ingot. Of course, the composition of the material added to the melt is substantially the same as the composition of the withdrawn ingot. Accordingly, an ingot is obtained having a composition which is relatively constant from one end to the other, an achievement which has been heretofore impossible to accomplish. In other words, an extended portion of the crystal has a useful range of composition. According to present day procedures, one would need an indefinitely long crystal to obtain a substantial amount of usable material from a single crystalline ingot. In other words, my procedure now makes it possible to obtain a single-crystal ingot which has only a small portion of waste material therein. Therefore, fewer crystal growing cycles are needed in order to provide the same quantity of

usable crystalline material, and the crystal growing techniques are much simplified because the temperatures may be held at a constant level at the liquid-solid interface.

Therefore, it is an object of the present invention to provide a single-crystal ingot having optimum characteristics from substantially one end to the other with a relatively small amount of waste or unusable material at either extremity, thereof.

It is a further object of the present invention to provide a method of growing single-crystal ingots wherein fewer growing cycles are necessary in order to obtain a given quantity of usable crystalline substance.

It is still a further object of the present invention to provide apparatus for growing the improved crystals as set forth herein.

The invention may be more easily and fully comprehended with reference to the accompanying drawing in which:

The figure is a vertical sectional view of a crystal growing apparatus particularly adapted for carrying out the present invention.

The improved process of the present invention is conveniently carried out in the crystal growing apparatus as illustrated in the accompanying drawing. Accordingly, there is provided a crystal growing assembly generally designated **10** which includes a crucible system **11** and crystal pulling mechanism generally designated **12** mounted within the shell or housing **14**. Metal feeding means **15**, heating coils **16**, and inert gas supply and exhaust tubes **17** and **18** respectively are also included in the system, and contained at least partially within the housing **14**. The crucible system generally designated **11** includes an inner container **20** surrounded and spaced from an outer shell **21**. The space between the inner and outer shells **20** and **21** defines an annular chamber as at **22**. Spaced ribs **24** are provided in the annular chamber **22** in order to hold the inner and outer shells **20** and **21** respectively in relatively spaced relationship. The inner container **20** is provided with a hole or port at **25** which provides communication between the inner chamber **26** and the outer annular chamber **22**. The crucible system **11** is mounted on the plate **28** which is situated on the shaft **29** and adapted for axial rotation therewith. Shaft **29** is adapted for axial rotation in the bearing **29A**.

The crystal pulling mechanism **12**, includes a pulling shaft **30** which is provided with a seed crystal retaining member **31** adapted to retain a seed crystal **32** by any convenient means, such as, for example, the set screw **33**. In operation, the ingot **35** is fused onto the seed crystal **32** and an extended ingot is formed or grown as the crystal pulling mechanism **12** is moved in the direction of the arrow **36** at a proper rate for growing or forming of the ingot **35**.

The crucible **11** is heated by the induction heating coils **16**, which are supplied with high frequency energy from an external source of conventional or well known design, not shown. The coils **16** are provided with cores **37** through which a suitable coolant, such as water, may flow.

The metal feeding means **15** includes a hopper member **40** containing a quantity of finely divided semi-conductor metal as shown at **41**. Control means, such as the damper **42**, are provided in the shaft **43** which extends from the hopper **40** to a point directly above the annular melting chamber **22**. Control means **42** are adapted to permit passage of solid material into the chamber **22** at a rate substantially equal to the rate at which material is drawn from the system in the form of the crystalline ingot **35**, thereby maintaining the quantity of metal within the crucible system **11** at a constant level at all times, even when the crystalline ingot is being pulled.

The improved process of the present invention may be conveniently carried out in the apparatus described hereinabove as follows. In operation, the crucible is filled with a charge of doped germanium having a resistivity which is lower than that desired in the grown crystalline ingot product. Since in germanium the ratio between impurity content in the solid phase to that in the melt, the segregation constant, is very low, a charge having a bulk resistivity substantially lower than that desired in the ingot is utilized. In other words, the impurity content of the charge is higher than that desired in the ingot. The charge is heated to a surface temperature of 940° F. and the crucible is then set into rotation about its axis, along with the shaft **29**. At this time, the seed crystal **32** is lowered and placed in contact with the surface of the melt, permitted to remain there for about 30 seconds, or until the crystal commences to form about the seed, at which time the seed crystal is slowly withdrawn, at a rate such that the crystalline ingot **35** forms thereon. The shaft **30** is drawn upwardly at a relatively constant rate, that is, at a rate substantially equal to the rate of forming of the crystalline ingot. For germanium, this rate is about 25 mils per minute at a surface temperature of 940° F. and with the crucible rotating at about 150 r.p.m. When the crystalline ingot being withdrawn from the melting zone **26** reaches an optimum composition as indicated by its resistivity, new material having a resistivity or impurity content substantially equal to that of the withdrawn ingot **35** is added to the melting zone **22** through the conduit or shaft **43** which extends from the hopper **40**. The proper times for adding new material to the melt is readily determined by practice. This new material is permitted to melt under the influence of the induction heating coils **16**, and under static pressure influence, eventually passes through the port **25** into the molten zone **26** of the inner crucible **20**.

It is preferable that the new material added to the melting zone **22** be permitted to reach a sufficiently high temperature for the period of time necessary for the material to become thoroughly molten and thereby lose its memory of crystallization, before it reaches the port **25**. In practice, it may be necessary in some instances to commence the pulling of a crystal before additional new material is added to the melting zone **22**. This would occur in instances where the crystal ingot being pulled has an original resistivity which is higher than that desired in the final product. It is important that the addition of new material is maintained substantially at the rate of withdrawal of material in the form of the crystalline ingot, the volume of metal in the crucible remaining substantially constant. This insures that the resistivity of the crystalline ingot as it is withdrawn will likewise remain constant.

Example

In order to prepare a crystalline ingot having a desired resistivity of from, for example, 4 to 6 ohm-centimeters, the crucible **11** is filled with a charge of n-type antimony doped germanium having a bulk resistivity of about 300 times that desired in the crystal. Of course, other doping substances may be utilized, such as arsenic, phosphorous, bismuth, indium or the like. The charge is then heated to a surface temperature of 940° F. and the seed crystal immersed a distance of 1/32 inch into the surface of the melt contained in the molten zone **26** of the crucible **11**. The seed crystal is permitted to remain in contact with the surface of the melt for about 30 seconds before rotation of the crucible is commenced, rotation is begun and a slow, constant withdrawal of the ingot is then started. For a temperature of 940° F., the ingot is withdrawn from the crucible at a rate of about 1½ inches per hour, and an ingot having a diameter of between 1 and 2 inches is formed. The segregation constant for this material is 0.003 for a non-agitated solution and 0.005 for a solution agitated and a crystal pulled at the rate set forth in this example. Upon commencement of withdrawal of the ingot from the melt, control member **42** is opened and additional material **41** comprising bulk germanium n-type, doped with antimony to a resistivity of from 4 to 6 ohm-centimeters is permitted to enter the system by way of the melting zone **22**. This addition of material is closely controlled at a rate substantially equal to the rate of withdrawal of material from the crucible system in the form of an ingot, and the bulk composition of this substance is substantially the same as the composition of the ingot.

Although specific reference has been made to germanium in this apparatus, the method is equally applicable to silicon and other metallic systems. As a slightly modified procedure in accordance with the present invention, it is possible to obtain an elongated crystal having a composition which varies over a desired impurity range by varying the rate of addition or composition of the addition material. In this regard new material having a composition substantially equal to that desired in the final crystal may be added to the melt as the ingot is withdrawn. Of course, as the drawing of the ingot is continued, the composition of the ingot will approach that of the added material, and close control of product composition is therefore possible. This composition control may also be achieved by the rate at which new material is added to the melt, since generally the composition of the melt will be more heavily contaminated than that of the ingot drawn therefrom. Therefore the ingot composition will approach a more heavily contaminated level as the quantity of the melt decreases due to lower or no addition of new material to the melt. This feature may be utilized for varying the composition of the ingot by a controlled addition of new material at a rate which varies from the rate of withdrawal.

Although various specific embodiments of the invention herein have been disclosed, it will be understood that there is no intention to limit the scope of the present invention to these specific embodiments alone, since they are used for purposes of illustration only. Many details of composition and procedure may be varied without departing from the principles of this invention. It is therefore not my purpose to limit the patent granted on this application otherwise than necessitated by the scope of the appended claims.

I claim as my invention:

1. The method of growing a uniformly oriented body of a semiconductor material selected from the class consisting of germanium and silicon and including a substantial portion with a uniform and predetermined concentration of a certain doping impurity dispersed therethrough from a melt of said semiconductor material including a concentration of said doping impurity which is greater than said predetermined concentration, said method comprising withdrawing said body from said melt at a predetermined rate, and maintaining said melt at constant volume and constant concentration of said doping impurity after said body has acquired said predetermined concentration at the interface with said melt by simultaneously adding new material to said melt at a rate equal to the rate at which the material is being withdrawn from said melt in the formation of said body and melting said new material in said melt, said new material consisting essentially of said semiconductor material and said doping impurity, with the concentration of said doping impurity in said new material being equal to said predetermined concentration.

2. The method of growing crystalline ingots of a semiconductor material selected from the class consisting of germanium and silicon and having a controlled first predetermined concentration of a certain doping impurity which method includes providing a melt of said semiconductor material together with a second predetermined concentration of said certain doping impurity, said second predetermined concentration of said certain doping im-

purity being greater than said controlled first predetermined concentration thereof, and withdrawing an ingot from said melt at a predetermined rate, a substantial portion of which ingot contains said certain doping impurity in said controlled first predetermined concentration while maintaining the volume of the melt and the concentration of said certain doping impurity therein constant after said body has acquired said predetermined concentration at the interface with said melt by simultaneously adding to the melt additional amounts of said semiconductor material and said certain doping impurity at a rate equal to the rate at which the material is being withdrawn from the melt in the formation of said ingot and melting said additional semiconductor material, the concentration of said certain doping impurity in the newly

added materials being equal to said controlled first predetermined concentration.

3. The method as set forth in claim 2 being further characterized in that said semiconductive substance is germanium.

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