March 22, 1966 J. L. VAN CAKENBERGHE 3,241,925

APPARATUS FOR GROWING SOLID HOMOGENEOUS COMPOSITIONS

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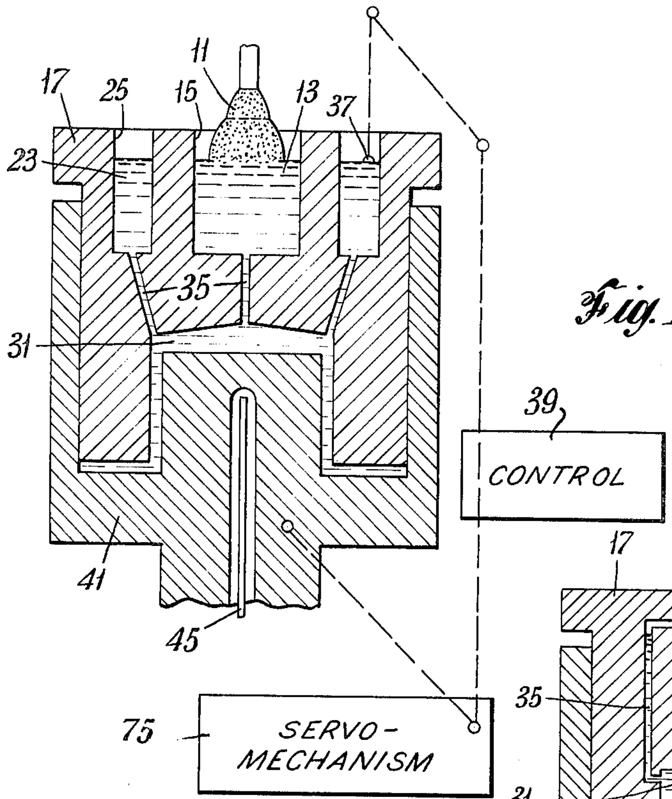

Fig. 1.

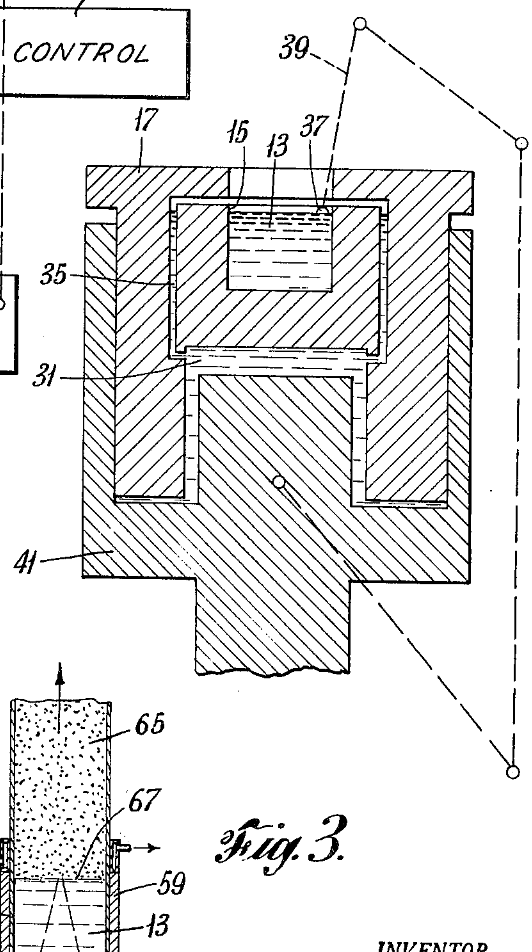

Fig. 2.

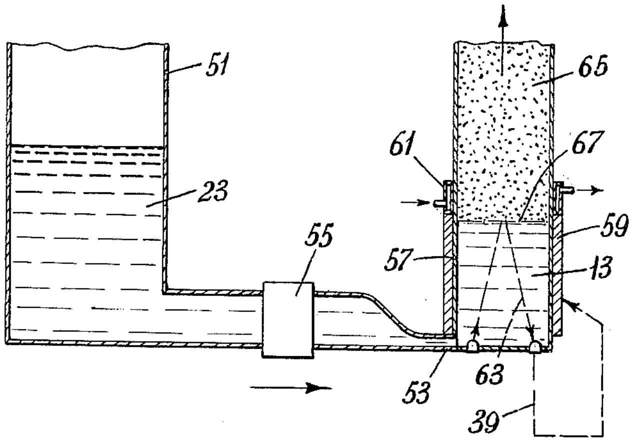

Fig. 3.

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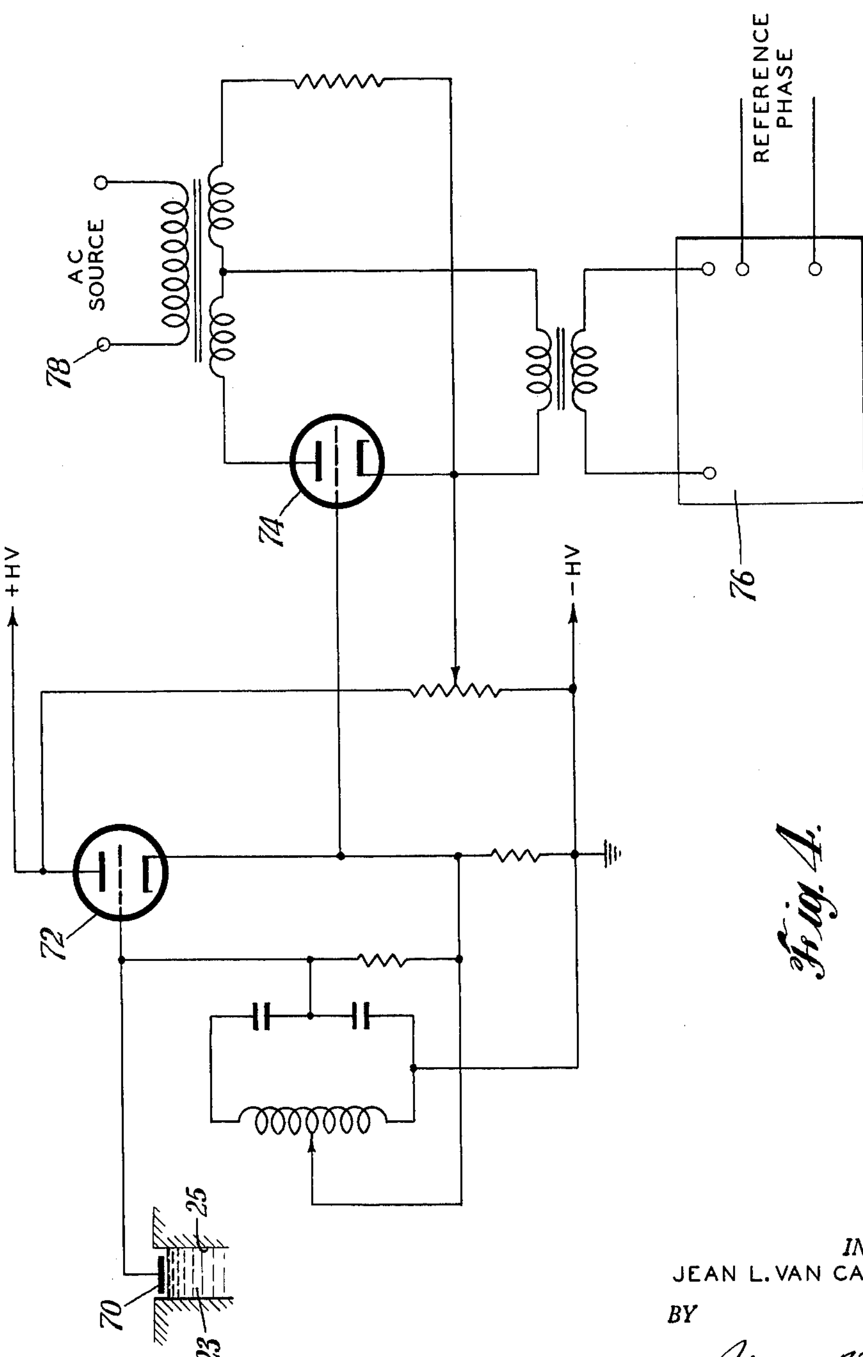

Fig. 4.

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United States Patent Office

3,241,925
Patented Mar. 22, 1966

3,241,925

APPARATUS FOR GROWING SOLID HOMOGENEOUS COMPOSITIONS

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Filed Aug. 19, 1960, Ser. No. 50,673
2 Claims. (Cl. 23—273)

The present invention relates to apparatus for growing solid, homogeneous compositions and, more particularly, to apparatus for growing solid, homogeneous compositions from a melt of constant volume.

Heretofore, the preparation of a solid solution from a melt consisting of dissimilar materials has presented several problems. One of the main difficulties has been the fact that a heterogeneous distribution of matter usually occurs during the freezing process because the solid portion which freezes first has a different composition from the portion freezing at the end. As a result, the physical properties, such as the electrical resistance, are not constant throughout the length of the solid material. Obviously, such a variation in properties is not tolerable where the solid material is to be employed in uses such as semiconductor elements.

Several techniques have heretofore been suggested for preparing homogeneous compositions. One such process is the large melt technique, wherein a single crystal is grown from a large melt which contains many times the amount of material desired in the final crystal. This process, however, requires a relatively large melt, which increases both the probability of contamination of the pure material in prolonged or repeated firings, and the size and complexity of the furnace.

Another process previously proposed is the zone leveling technique, wherein an apparatus similar to that used in zone refining is utilized to grow a single crystal in a horizontal direction. If the molten zone length is successively decreased during this process, a fairly homogeneous crystal can be produced. In practice, however, precise control of the molten zone length is difficult to obtain, and slight variations in the molten zone during the process produce resistivity variations in the resultant crystal.

In the floating crucible technique, single crystals are "pulled" from an inner crucible floating in a melt of material contained in a larger concentric crucible. The inner crucible has a hole through its bottom so that it will float in the outer melt at a predetermined equilibrium depth as material is withdrawn from the inner melt. A seed crystal is then dipped into the inner melt, and a crystal is grown by the usual seed-pulling technique. Since the floating equilibrium is an essential condition, however, each run requires a careful adjustment to avoid a loss of equilibrium by friction, and the mass of the floating crucible must be standardized every time a new melt is used. Also, if the melt contains a volatile element, the floating equilibrium will be easily disturbed. Furthermore, in the floating crucible process it is difficult to maintain the melt in the inner crucible at a constant temperature because the crucible is progressively lowered during the process.

It is, therefore, the main object of the present invention to provide an apparatus for growing solid, homogeneous compositions from a melt of constant volume, which does not require frequent calibrations.

Another object of the invention is to provide an apparatus for growing solid, homogeneous compositions wherefrom ingots of any size and shape may be obtained.

Other aims and advantages of the present invention

will be apparent from the following description and appended claims.

In the drawings:

FIGURE 1 is a vertical cross-sectional view of a preferred embodiment of the present invention;

FIGURE 2 is a vertical cross-sectional view of a modified embodiment of the invention; and

FIGURE 3 is a vertical cross-sectional view of another modified embodiment of the present invention.

In accordance with the present invention, there is provided an apparatus for growing a solid, homogeneous composition from a body of molten material comprising, in combination, means for withdrawing the solid composition from the body of molten material; detecting means responsive to any variation in the volume of the body of molten material; controlling means responsive to the detecting means; and compensating means responsive to the controlling means for compensating for any variation in the volume of the body of molten material.

The present invention provides a novel apparatus for growing solid, homogeneous compositions from a melt of constant volume. The solidification is achieved by withdrawing (by pulling or by extrusion) the melt or a portion of it from a crucible so as to form the desired solid. The withdrawing means is preferably a seed attached to a rod, which is dipped into the melt. The conventional technique for seeding and growing crystals is well known in the art and is described in detail in Chapter 10 of An Introduction to Semiconductors by W. C. Dunlap.

In order to maintain the melt at a constant volume and to insure homogeneous properties in the withdrawn solid composition, means are provided for automatically replenishing the melt from a supply of molten material having substantially the same composition as that of the withdrawn solid. It is especially important that the replenishing material have a composition corresponding to the composition of the withdrawn solid, which is usually not the same as the composition of the melt from which the solid is grown. For example, in germanium the segregation constant (the ratio of impurity content in the solid phase to the impurity content in the liquid phase) is very low, so the melt from which the solid is grown should have a resistivity lower than that desired in the solid. In other words, the impurity content of the melt should be higher than that desired in the solid.

Since the rate of withdrawal may vary in some cases, and it is essential to maintain the growing melt at a constant volume, the present invention provides a means for detecting any variation in the volume of the growing melt. Any change in the volume of the melt is immediately detected by the detecting means, which then activates a compensating means through an appropriate feedback control system. The compensating means then maintains the melt at a constant volume either by controlling the rate of flow of the replenshing supply, or by controlling the temperature or some other variable of the melt itself. Any convenient feedback control system, such as a hydraulic system, a chain of relays and magnetic valves, or an electrical feedback system, can be used between the detecting means and compensating means.

The apparatus of the present invention will now be described in greater detail by referring to the embodiments of the drawings. In the preferred embodiment of FIGURE 1, a solid, homogeneous composition **11** is withdrawn from the inner melt **13** contained in the crucible-like cavity **15** of the cylindrical vessel **17**. The solid composition **11** can be a solid solution, a crystalline material, or a single crystal. There are no limitations on the melt **13**, provided that the constituents are mixed in a proportion corresponding to the range of stability in the resultant solid. Some examples of solid compositions grown by the present process are germanium doped with arsenic, germanium doped with antimony, and an alloy of 30 percent copper and 70 percent nickel by weight. The solid can be withdrawn in the shape of bars, rods, plates, etc. by pulling the solidifying portion through a die fitted on top of the cavty 15.

The replenishing supply of molten material having the same composition as that of the solid composition 11 is contained in the outer annular cavity 25, which is concentric with the inner cavity 15, and in the recess 31 in the bottom of vessel 17. Since the concentric cavities 15 and 25 are both connected to the recess 31 by means of the capillary tubes 35, any decrease in the surface level of melt 13 results in a corresponding decrease in melt 23. Thus, any change in the volume of melt 13 is immediately detected by the detecting element 37 on the surface of the outer melt 23, and the compensating means 41 is instantaneously activated by the feedback controlling means 39, and servomechanism 75, as illustrated in FIGURE 4.

Referring to FIGURE 4 in the preferred embodiment of the invention the detecting element 37 is an electrode 70, and the desired control of the volume of melt 13 is achieved by maintaining at a constant value the electrical capacity of a system formed by the surface level of melt 23 and the electrode 70. This capacity is made part of a high-frequency oscillator 72 in such a way that any change in the capacity results in a change in the oscillation amplitude, which in turn is detected and used to polarize a tube or a thyratron 74. The tube or thyratron 74 is connected to an alternating current source 78 in such a way that the phase and amplitude of the alternating current vary with the change in polarization of the tube 74, and thus with the position of the surface level of melt 23. This alternating current is supplied to a servomotor 76 which maintains melt 13 at a constant level by acting upon the compensating means 41.

Another method of detecting variations in the volume of melt 13 would be to shape cavity 25 in such a way that its bottom is an inclined plane, so that any variation in the volume of melt 13 would result in a variation in the surface area of the melt 23. Then if detecting element 37 were an optic device, any variation in the volume of melt 13 would be detected by the optic device and compensated for by an appropriate servomechanism.

In the preferred embodiment of FIGURE 1, the compensating means is a compressing means 41, which forces some of the replenishing material out of recess 31 into the cavities 15 and 25. Of course, if melt 13 is continuously withdrawn as solid composition 11, the compressing means 41 moves up continuously at a rate dependent upon the rate of withdrawal, and the replenishing supply is continuously forced into the cavities 15 and 25. Thus, the volume of melt 13 in cavity 15 remains substantially constant. Obviously, the composition of the replenishing material must be the same as that of the withdrawn solid if the composition of the solid is to be homogeneous. Thermocouple 45, located inside the compressing means 41, provides a constant check on the temperature of the molten material in recess 31.

Drawback of material from cavity 15 to recess 31 can be avoided by using a capillary tube 35 as shown in FIGURE 1 or by having the outlet of the connection between recess 31 and cavity 15 located above the melt level inside cavity 15, as shown in FIGURE 2. The only difference in the devices shown in FIGURE 1 and FIGURE 2 is that the former feeds the replenishing material into the bottom of cavity 15 by means of capillary tube 35, while the latter feeds the material directly into the top of cavity 15. In both cases the replenishing supply is added by a compressing means 41 which is activated by a feedback system 39. Since the detecting means 37 in the device shown in FIGURE 2 is directed

to melt 13 rather than an external melt, the detecting means 37 should be placed so as to leave open the entrances to the capillary tubes 35 and to avoid any contact with the solid composition 11.

A modified embodiment of the inventive apparatus is illustrated in FIGURE 3. Melt 23, held in container 51, is continuously forced through connection 53 at a constant rate by means of pump 55. From connection 53, the molten material passes into crucible 57, which is surrounded by heater 59. Any convenient heating means, such as a high frequency heating system, can be used as heater 59. Directly above heater 59 is a cooling jacket 61, which continuously freezes the molten material at a given-level inside the crucible 57. Any variation in this freezing level is immediately detected by a detecting means, such as by reflection of an ultrasonic beam 63. Just as in the hereinbefore-described embodiments, a feedback system 39 instantaneously activates a compensating means which corrects the volume of melt 13 to the constant value. In this embodiment of the invention, the compensating means is the heater 59, which controls the volume of melt 13 by controlling its temperature. The homogeneous ingot 65 is continuously removed above the freezing zone 67.

A homogeneous solid solution of bismuth, antimony, and tellurium was prepared in the device shown in FIGURE 1 with a hydraulic feedback control system. The solid obtained was a cylindrical rod with a diameter of 1.1 cm. and a length of about 20 cm. The crystals of the solid were oriented with their Z-axes perpendicular to the direction of pulling. The pulling rate was 0.5 mm./min. and the temperature of the crucible was maintained at 610° C.

The resultant rod was cut into ten pieces about 1 cm. long and the Seebeck coefficient was measured for each piece at 28° C. by the hot point method. The results given in the following table show that the physical properties of the product were substantially homogeneous throughout its length. The terminal pieces were discarded.

TABLE

Piece No.:	Seebeck coefficient in $\mu V/°$ C.
2	126.3
3	123.0
4	123.2
5	123.7
6	121.1
7	122.2
8	124.1
9	122.0

Apparatus for growing solid, homogeneous compositions from a constant volume of molten material is, of course, well known in the art. The novelty of the present invention lies in the combination of means by which the volume of the growing melt is kept constant, i.e., the detecting means which continuously detects any change in the volume of the growing melt, the controlling means which is responsive to the detecting means, and the compensating means which is responsive to the controlling means and compensates for any change in the volume of the growing melt. The apparatus of the invention is especially suitable for the preparation of homogeneous, solid solutions of semiconductor material or mixtures of semiconductor material with various compounds. The apparatus is also admirably suited for the preparation of single crystals of solid solutions which could not heretofore be prepared by any known method. The application of the invention is not restricted to the semiconductor field, but can be equally useful in the field of metallurgy.

The inventive apparatus is more reliable than apparatus of the prior art because it is automatic, and is more flexible because it does not require frequent calibration and does not limit the size or shape of the solid that can be withdrawn. Also, since the present apparatus is fed with material in the liquid state rather than in powder form, a pumping system, e.g., and electromagnetic pump, can be used to provide more accurate and more flexible feed control of the molten material.

What is claimed is:

1. Apparatus for growing a homogeneous solid composition comprising: an outer crucible and an inner crucible disposed concentrically within said outer crucible, the outer side walls of said inner crucible being in sliding contact with the inner side walls of said outer crucible, and the outer bottom wall of said inner crucible and the inner bottom wall of said outer crucible being spaced apart to define a recess therebetween; at least one capillary tube extending through the bottom wall of said inner crucible, said tube being sufficiently small to prevent drawback of molten material from said inner crucible into said recess; a body of molten material within said inner crucible; means for withdrawing a solid composition from the molten material in said inner crucible; a body of molten material having the same composition as said withdrawn solid within said recess between said crucibles; detecting means responsive to any variation in the volume of molten material in said inner crucible; control means responsive to said detecting means; means responsive to said control means and acting upon said crucibles to decrease the volume of said recess thereby replenishing any decrease in volume of molten material in said inner crucible by forcing molten material from said recess through said capillary tube and into said inner crucible.

2. Apparatus for growing a homogeneous solid composition comprising: an outer crucible and a stationary inner crucible disposed concentrically within said outer crucible, the outer side walls of said inner crucible being in sliding contact, with the inner side walls of said outer crucible, and the outer bottom wall of said inner crucible and the inner bottom wall of said outer crucible being spaced apart to define a recess therebetween; at least one capillary tube extending through the bottom wall of said inner crucible, said tube being sufficiently small to prevent drawback of molten material from said inner crucible into said recess; a body of molten material within said inner crucible; means for withdrawing a solid composition from the molten material in said inner crucible; a body of molten material having the same composition as said withdrawn solid within said recess between said crucibles; detecting means responsive to any variation in the volume of molten material in said inner crucible; control means responsive to said detecting means; means responsive to said control means and acting upon said outer crucible to decrease the volume of said recess thereby replenishing any decrease in volume of molten material in said inner crucible by forcing molten material from said recess through said capillary tube and into said inner crucible.

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