July 3, 1956 A. R. MOORE 2,753,280

METHOD AND APPARATUS FOR GROWING CRYSTALLINE MATERIAL

Filed May 1, 1952 2 Sheets-Sheet 1

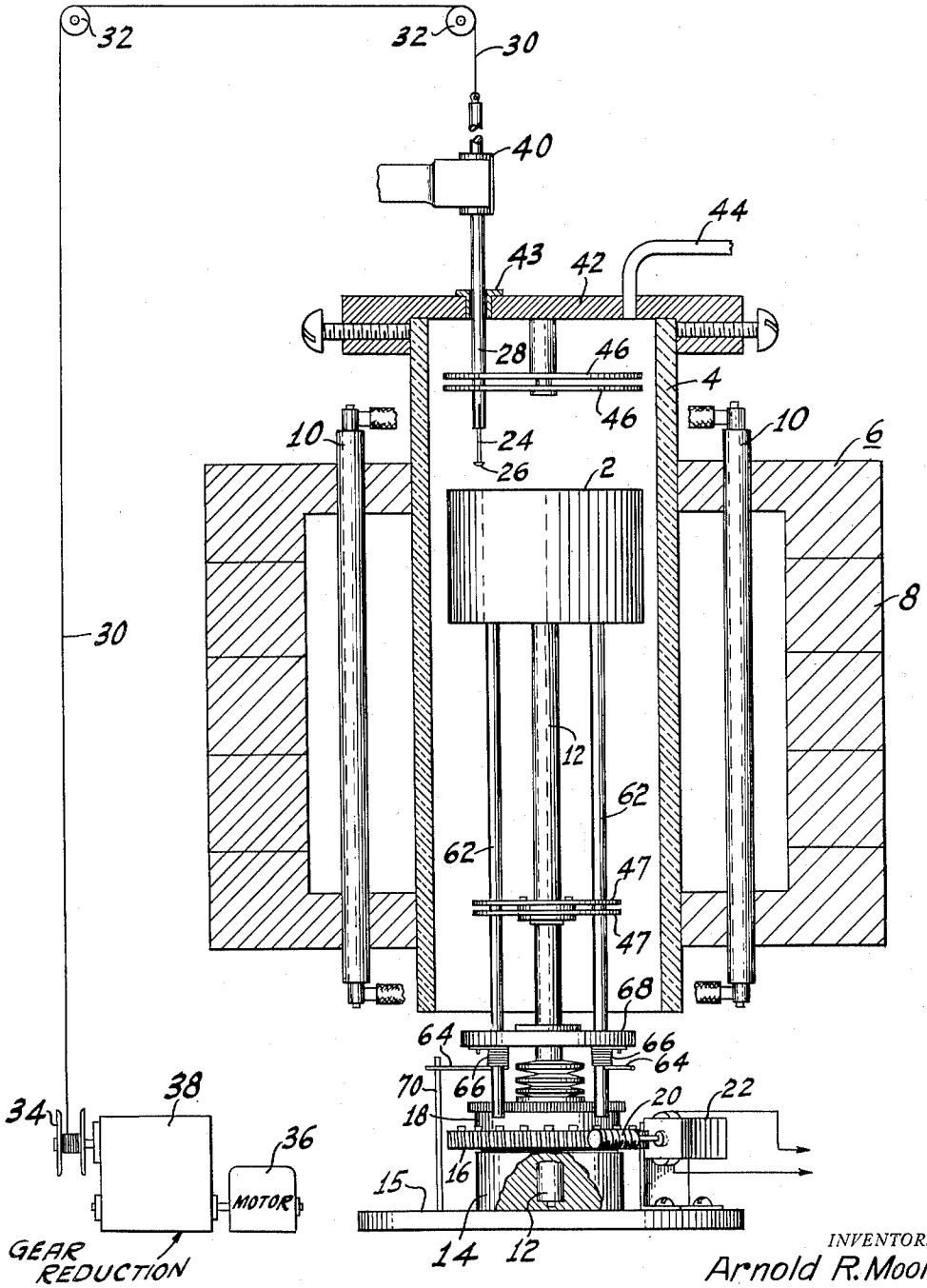


Fig_1

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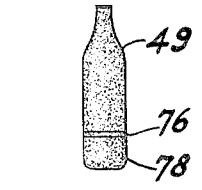


Fig_4

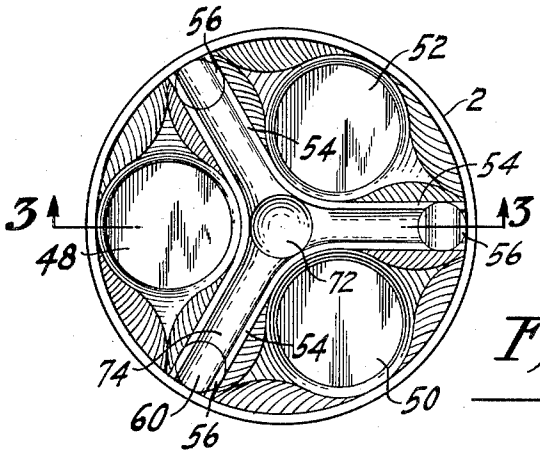


Fig_2

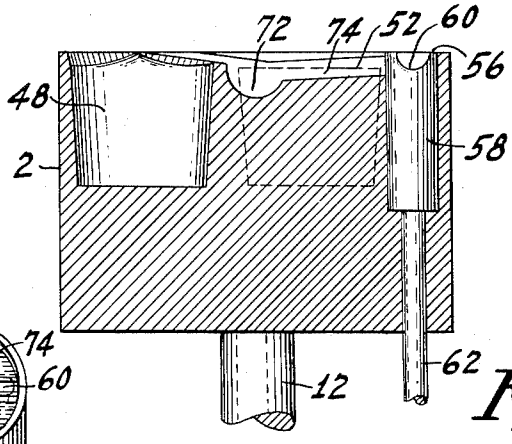


Fig_3

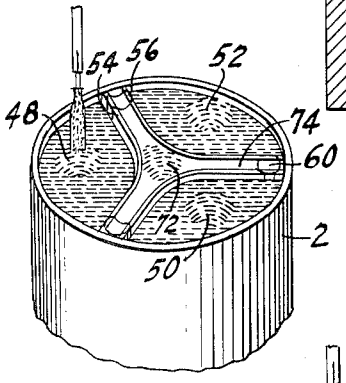


Fig_5

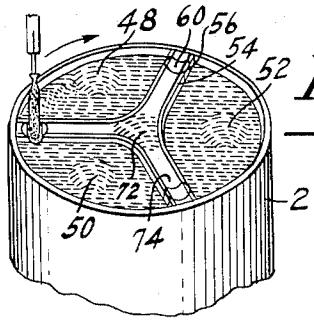


Fig_6

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METHOD AND APPARATUS FOR GROWING CRYSTALLINE MATERIAL

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The terminal 15 years of the term of the patent to be granted has been disclaimed.

17 Claims. (Cl. 148—1.5)

This invention relates to an improved method and apparatus for growing crystals from molten bodies of material and, more particularly, to an improved method and apparatus for growing a single crystal having zones of different compositions.

Methods of growing single crystals of considerable size of various substances have previously been known. One method of growing crystals is to bring a properly oriented seed crystal into contact with the surface of a molten body of a substance and then to very slowly withdraw the seed crystals from the melt at a rate of speed such that material from the molten body will adhere to the seed crystal thus causing the seed crystal to grow. The new crystal portion will continue to grow in length as long as the seed crystal is moved away from the surface of the molten body and as long as there is any material remaining to be used.

When applied to a particular material, such as germanium, this technique is usually carried out by maintaining a quantity of liquid germanium in a carbon crucible within an electric furnace having its temperature precisely controlled to within one degree centigrade, the furnace also being enclosed and supplied with an inert gaseous atmosphere. When a seed crystal of germanium is touched to the surface of molten germanium in a crucible maintained in this type of furnace and when the rate of withdrawal of the seed crystal is carefully maintained so as to balance the rate at which the germanium is crystallizing, crystals of considerable length can be grown.

It has now become desirable, however, to grow crystals of semi-conductors, such as germanium, having adjacent zones of slightly different composition. For example, it is desired to grow crystals having a zone, say of P-type material followed by a zone of N-type material and, perhaps, repeating this one or more times throughout the length of the crystal.

It has been known that N-type semi-conductor material such as germanium can be prepared by reducing germanium dioxide of a high degree of purity to produce elemental germanium. This elemental germanium can be put through one or more stages of further purification until the impurities remaining cause it to have a certain resistivity. Germanium obtained from usual commercial sources when purified and repurified in this manner usually turns out to be N-type material. N-type material can also be obtained by purifying and repurifying germanium until substantially all of the impurities have been removed, and then adding very small controlled amounts of certain elements which are known to impart N-type characteristics to the substance. Examples of elements which can be added to intrinsically pure germanium to produce N-type conductivity material are arsenic, antimony or any other element in the 5th column of the periodic table. On the other hand, P-type conductivity material can be prepared by first obtaining intrinsically pure germanium and then adding certain impurity elements such as indium or gallium.

The present invention, in brief, comprises a method

and apparatus for growing semi-conductor crystals having adjacent N-type conductivity and P-type conductivity zones by, first, withdrawing a seed crystal from a melt of one particular type, for example N-type, and then, without breaking contact between the growing crystal and the molten material, transferring it to a melt of P-type material, and continuing the growth of the crystal. This process may be repeated a number of times if desired.

One object of the present invention is to provide an improved method of growing crystalline material in which a single crystal is provided with zones of different composition.

Another object of the invention is to provide an improved method of growing germanium crystals having one or more P–N junctions therein.

Another object of the invention is to provide an improved method of introducing P–N junction into crystalline semi-conductors.

Another object of the invention is to provide an improved apparatus for growing crystals from molten material.

Another object of the invention is to provide improved apparatus for growing crystals with regions of different impurity content.

Still another object of the invention is to provide improved apparatus for growing crystals of germanium semiconducting material having any desired number of P–N junctions incorporated therein.

These and other objects will be more apparent and the invention will be more readily understood from the following detailed description and the accompanying drawing of which,

Figure 1 is an elevation view, partly in section, of one form of apparatus constructed in accordance with the present invention,

Figure 2 is a plan view of the crucible portion of the apparatus of Figure 1;

Figure 3 is a section view taken along the line 3—3 of Figure 2,

Figure 4 is an elevation view of a crystal such as might be grown in the apparatus of the preceding figures,

Figure 5 is a top perspective view of the crucible portion of the apparatus of the preceding figures showing the relative positions of the individual crucibles and other portions of the crystal growing apparatus during an initial stage of the process of the present invention, and

Figure 6 is a view similar to Figure 5 during an intermediate stage of the crystal growing process.

Referring now to Figure 1, one form of apparatus which is suitable for carrying out the method of the present invention comprises a cylindrically shaped carbon crucible **2** disposed within a quartz tube **4**, the tube, in turn, being located within an electrical furnace **6**. The furnace includes firebrick walls **8** and a number of Globar heating units **10** symmetrically spaced around the quartz tube. Means, not shown, are provided for supplying regulated current to the Globar units.

The carbon crucible is rotatably mounted on top of a vertically positioned shaft **12**. The shaft is provided with a bottom bearing **14** mounted upon a base platform **15** and with means for rotating the shaft. The means for rotating the shaft comprises a gear wheel **16**, engaged with a worm driving gear **20** and mounted on the outer periphery of a sleeve **18** connected to the lower end of the drive shaft **12**. The worm gear is connected to a motor drive mechanism **22** which may be controlled by suitable switching means not shown.

The crucible portion of the apparatus also contains various chambers, canals, and valves which will be more particularly described later.

Another part of the apparatus is the means for withdrawing a seed crystal from a bath of molten material

disposed within the crucible portion of the apparatus. This part of the apparatus comprises a thin stainless steel shaft which serves as a crystal mount 24 for holding a seed crystal 26 and a vertically disposed stainless steel shaft 28 to the lower end of which the crystal mount is connected. In order to move the entire assembly consisting of the shaft 28, the crystal mount 24, and the seed crystal 26 very slowly at a uniform rate of speed in a vertical direction, one end of a thin wire 30, which may be of Phosphor bronze is attached to the upper end of the shaft 28. The wire is passed over two direction-changing pulleys 32 and its other end is then connected to a drum 34 which is rotatably driven by a motor 36 through a train of speed-reducing gears 38.

To maintain the shaft 28 in its vertical position, it is provided with a guide sleeve 40.

Means are also provided for maintaining a suitable gaseous atmosphere around the carbon crucible within the quartz tube. To prevent access of air, the top end of the quartz tube is provided with a lid 42. The crystal-pulling shaft 28 is inserted through a bushing 43 in this lid. A tube 44 inserted through the lid permits introduction of any desired gas. Radiation baffles 46, suspended from the lid, are provided to lower heat losses through the lid. Additional radiation baffles 47 are also provided below the crucible 2. These are attached to the shaft 12.

With particular reference to Figures 2 and 3, the crucible portion of the apparatus will now be described in more detail. The crucible 2 is a block of carbon out of the upper side of which have been hollowed three small crucibles or vessels 48, 50, and 52 symmetrically disposed 120° apart about the carbon block. These smaller crucibles are separated by walls of carbon 54 which are left standing when the smaller crucibles are hollowed out. Thus, normally, molten material in each of the three smaller crucibles is kept separated from the others.

Between the smaller crucibles are valves 56. Referring now more particularly to Figures 1, 2, and 3, each valve comprises a solid cylinder of carbon 58 seated within a correspondingly shaped hollowed out portion of the large carbon block. The top of each valve cylinder is provided with a deeply scored channel or canal 60. The valve cylinder is free to rotate within the valve seat. Means for rotating each valve comprises a long shaft 62, which may also be of carbon, connected to the bottom of each carbon valve cylinder. These valve shafts extend downward and outside the furnace. Disposed near the bottom of each of the valve shafts is a lever 64 projecting horizontally out of the shaft. In order to maintain each valve in a normally closed position except when it is desired to open it, each of the valve shafts is provided with a biasing spring 66 mounted upon a support plate 68. The support plate is mounted upon the crucible drive shaft 12 and also serves as a support and positioning means for the valve shafts 62.

For opening and closing each valve automatically at a particular point in the operations cycle of the apparatus, there is provided a vertically mounted tripping bar 70 adapted to engage each of the levers 64 as the crucible portion of the apparatus is rotated. The operation of this portion of the apparatus will more particularly be described later when a complete operations cycle is given.

The crucible of the apparatus is also provided with means for receiving undesired portions of the melt which are produced during an operations cycle. This means comprises a central chamber 72 having radial channels 74 located between the crucibles and extending one to each valve. When the valves are in their normally closed position, their fluid channels 60 connect with the radial channels 74 leading to the waste receptacle.

A preferred example of the method of growing a crystal in accordance with the teachings of the present invention will now be given. Preliminary to starting to grow a crystal, each of the small crucibles is provided with a charge of material of desired composition. If a crystal of germanium is to be grown, the first crucible 48 is given a charge of germanium of, say, 1–2 ohm-cm. N-type material. The second crucible 50 is given a charge of, say, .05–.1 ohm-cm. P-type material. The third crucible 52 is given a charge of, say, .001 ohm-cm. N-type material. A seed crystal 26 oriented in a particular desired manner is attached to the bottom end of the crystal mount 24. Argon gas is admitted through the tube 44 and the furnace is heated in order to melt the charges of germanium in the small crucibles. The temperature of the molten germanium is carefully maintained substantially constant within about 1° C. at a temperature of about 950° C. With all three valves 56 closed, the seed crystal is carefully lowered until it touches the surface of the molten germanium in the first of the smaller crucibles 48. The motor 36 is then started and the wire 30 is slowly wound around the drum thus raising the shaft 28 and also the seed crystal. The gear ratio of the speed-reducing gears 38 is chosen such that the motor will wind up the wire at a rate calculated to raise the seed crystal at a rate of, say, 1 mm. per minute. This rate will vary for different materials, different furnace constructions, different melt temperatures, and other factors. In any case, the rate of withdrawal of the seed crystal must be adjusted so that it just balances the rate of crystallization of the molten material. If the withdrawal rate is too rapid, the diameter of the growing crystal will become progressively smaller, and it may break away entirely from the melt. If the rate of withdrawal is too slow, the seed crystal may be lost, or the material may start to crystallize in a shape which is not desired.

After a desired length 49 of crystal has been grown, as, for example, the length shown in Figure 5, preparation may then be made for transferring the growing crystal to the next one of the smaller crucibles 50. Without stopping the withdrawal of the crystal from the melt, the motor drive mechanism 22 is activated causing rotation of the support and drive shaft 12 and the large carbon crucible 2.

Referring to Figures 5 and 6, as the large carbon crucible is slowly rotated in a clockwise direction, the valve between small crucibles 48 and 50 is automatically opened permitting some of the molten material from the two adjacent smaller crucibles to flow into the scored out passage of the valve and form a continuous fluid path between the two smaller crucibles.

The opening of the valve is brought about when the horizontally extending lever 64 attached to the lower end of the shaft 62 which rotates the valve, strikes the tripping bar 70 mounted on the base platform of the apparatus.

With the valve open, and the large crucible continuing to rotate, the lower end of the growing crystal passes through the valve passage and into the next crucible 50 without breaking contact with the molten material. As soon as the growing crystal has passed through the valve passage, the lever 64 slides past the tripping bar and the tension on the biasing spring 66 causes the valve to snap back into its normally closed position.

The molten material picked up by the valve passage when the valve was open, is permitted to run down one of the radial passages 74 into the waste receptacle 72 at the center of the large crucible. Since this waste material is a mixture of the molten material in the two adjacent crucibles, it is not desired to have it flow into either one of the small crucibles. Flowing of the molten material into the waste receptacle is aided by having the scored out passage 60 of the valve inclined at a slight angle toward the center of the large crucible when the valve is normally closed. The radial passages 74 are also similarly inclined.

With the apparatus shown and described, transfer of the growing crystal from one of the smaller crucibles to the next, can be accomplished in about one second.

With the seed crystal and the growing crystal now suspended over the second of the smaller crucibles **50**, the withdrawal of the seed crystal is continued and an additional length of crystal **76** is grown from the material. The width of the region grown in the second crucible can, of course, be controlled by the length of time the growing crystal is permitted to remain in this crucible. When a region of desired width has been grown, the large crucible is again rotated in a clockwise direction, the valve between the crucibles **50** and **52** is automatically opened, and the growing crystal is transferred to the third crucible **52**. In the third crucible, another region **78** of desired width is grown. After this last mentioned region is grown, the growing crystal may be raised out of the melt and the operation terminated or, if desired, the entire sequence of operation may be repeated and additional zones grown on the crystals.

By the method which has just been described, crystals can be grown having any number of adjacent P-type and N-type regions since the large crucible may be made to contain any desired number of smaller crucibles. It has furthermore been found that when germanium crystals are grown in this manner, crystals of excellent quality can be obtained and sections can be cut out which exhibit good rectification properties and other properties which are associated with P–N junctions.

Various changes and modifications can be made in the method and apparatus of the present invention without departing from the scope thereof. With regard to the method, it can be applied to any material capable of being crystallized from a melt by withdrawal of a seed crystal. Another example of this type of material is silicon. The compositions of the melts in the various smaller crucibles may be varied as desired. Although the method has been described in connection with growing a crystal with N–P–N type regions, it can also be adapted to growing a crystal with a P–N–P section or for growing crystals in which the different zones vary in other respects so far as composition goes.

The temperature at which the crucible portion is maintained depends upon the material being handled. In the case of germanium, temperature is usually held substantially constant within a range of about 930° to 950° C. For other materials, the temperature differs from these figures. Also it may be desirable, in some cases, to vary the temperature somewhat when the growing crystal is transferred from one of the smaller crucibles to another. This can easily be done with simple current control apparatus of conventional type.

Any type of desired atmosphere can also be used within the furnace while the crystal is being grown. Other inert gases such as helium or neon may be used, for example, or, if desired, a vacuum may also be used in the growing of germanium crystals. In the growing of still other materials, other types of atmosphere may be desired.

Certain modifications can also be made in the apparatus without departing from the scope of the invention. For example, the shaft **28** to which the crystal mount is attached may be rotated as the seed crystal is raised from the melt with the growing crystal attached to it. This causes the growing crystal to be rotated as it grows. Rotation of the shaft can be easily accomplished by a gear arrangement very similar to that used to rotate the supporting shaft of the large carbon crucible **2**. Although automatic operation has been described, it is obvious that the large carbon crucible could be rotated by hand and that the valves need not be operated automatically. By including a window in the lid **42**, for observation purposes, the valves could be hand operated at the proper times.

Without much deterioration in the quality of the product, the radial channels **74** and the waste receptacle can be omitted and, for some purposes, these are not used.

The number of smaller crucibles can be multiplied as

desired provided the apparatus is scaled in size accordingly.

There has thus been described a method and apparatus which can be applied especially to the growing of crystals of semi-conducting material having successive zones of P-type and N-type material. The width of the zones can be made very thin and the crystals which result can be made into junction type devices which are now well known in the art.

I claim as my invention:

1. A method of producing crystalline material having zones of different composition comprising withdrawing at a predetermined rate of speed a seed crystal from a vessel containing a molten material having a certain impurity content so as to grow a crystal portion of said material attached to said seed crystal, and, after said growing crystal portion has attained a desired length, transferring said growing crystal portion to another vessel containing said material having a different impurity content, said transfer being effected without breaking contact between the growing crystal portion and the molten material, and continuing the growth of said growing crystal portion.

2. A method of producing crystalline material having zones of different composition comprising dipping a seed crystal of a particular material into a molten body of said material, said material having a particular impurity content, slowly withdrawing said seed crystal from said molten body at a predetermined rate so as to grow a crystal portion of said material attached to said seed crystal, and, after said growing crystal portion has attained a desired length, transferring said growing crystal portion into contact with another molten body of said material having a different impurity content without breaking contact between said growing crystal portion and the molten material, and continuing to withdraw said growing crystal portion to continue the growth thereof.

3. A method of growing a crystal of semi-conducting material having a P–N junction included therein, comprising bringing a seed crystal of said material into contact with a molten body of said material, said material being either P-type conductivity or N-type conductivity with respect to impurity content, withdrawing said seed crystal from said molten body at a predetermined rate so as to grow a crystal portion of said material attached to said seed crystal, and, after the growing crystal portion has attained a desired length, transferring said growing crystal portion into contact with a different molten body of said material which is of opposite type to said first mentioned body, said last mentioned contact being effected without breaking contact between said growing crystal portion and said molten material, and continuing to withdraw said growing crystal portion to continue the growth thereof.

4. A method according to claim 3 in which said material is germanium.

5. A method according to claim 4 in which the first molten body is N-type conductivity and the second molten body is P-type conductivity.

6. A method according to claim 5 in which the first molten body is of N-type conductivity germanium having a resistivity of 1–2 ohm-cm. and the second molten body is of P-type conductivity germanium having a resistivity of .05–.1 ohm-cm.

7. A method of producing crystalline material having zones of different composition comprising bringing a seed crystal into surface contact with a first body of molten material having a particular impurity content, withdrawing said seed crystal at a predetermined rate so as to grow a crystal portion of said material attached to said seed crystal, after said growing crystal portion has attained a desired length, transferring said growing crystal into contact with a second molten body of said material having a different impurity content without breaking contact between said growing crystal and the molten material, continuing to withdraw said seed crystal and said growing

crystal portion until another desired length of crystal has been grown, and then transferring said growing crystal portion into contact with a third molten body of said material having an impurity content different from that of said second body, and continuing growth of said growing crystal portion until a further desired length has been grown.

8. A method according to claim 7 in which said first molten body is composed of N-type conductivity semi-conducting material, said second molten body is composed of P-type conductivity semi-conducting material, and said third molten body is composed of N-type conductivity semi-conducting material.

9. A method according to claim 8 in which the material in each of said bodies is of increased resistivity compared to the preceding body of the series.

10. A method according to claim 9 in which said material is germanium.

11. Apparatus for growing crystals of a particular material comprising a plurality of vessels for containing quantities of said material, means for heating said vessels to a temperature required to maintain said material in a molten state, means providing continuous fluid paths for said molten material between at least some of said vessels, means for suspending a seed crystal over successive ones of said vessels, and means for moving said crystal vertically relative to said vessels at a desired rate of speed.

12. Apparatus according to claim 11 including valve means for selectively opening and closing each of said fluid paths.

13. Apparatus according to claim 12 in which each of said valves is constituted by a rotatable member having an open-top channel therein adapted to serve as a part of one of said fluid paths when said valve is in open position.

14. Apparatus according to claim 13 including a waste material receptacle, and means connecting said valve channels to said receptacle when said valves are in their closed positions.

15. Apparatus for growing crystalline material, comprising a plurality of crucibles for containing quantities of said material, means rotatable about a central axis for holding all of said crucibles, means for heating said crucibles to a temperature required to maintain said material in a molten state, open-top channel means providing continuous fluid passages between said crucibles, means for suspending a seed crystal over one of said crucibles, and means for moving said crystal vertically at a predetermined rate relative to said crucibles.

16. Apparatus according to claim 15 in which said rotatable holding means is a carbon block and said crucible and said channel means are hollowed out below a surface of said block.

17. Apparatus according to claim 11 including means for transferring a growing crystal portion attached to said seed crystal, from one of said vessels to another along one of said paths without breaking contact between said growing crystal and said molten material.

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