

[72]	Inventor	Sidney Glenn Parker Dallas, Tex.
[21]	Appl. No.	2,751
[22]	Filed	Jan. 14, 1970
[45]	Patented	Jan. 11, 1972
[73]	Assignee	Texas Instruments Incorporated Dallas, Tex.

FOREIGN PATENTS

482,096	7/1936	Germany.....	23/301
148,016	9/1962	U.S.S.R.	

OTHER REFERENCES

Fischinger, A Floatation of Growing Large Single Crystals, Aug. 1969 Journal of Chemical Education, page 486.

Primary Examiner—Norman Yudkoff

Assistant Examiner—S. Silverberg

Attorneys—Samuel M. Mims, Jr., James O. Dixon, Andrew M. Hassell, Harold Levine, Melvin Sharp, William E. Hiller and John E. Vandigriff

**[54] GROWTH OF CRYSTALS AT A UNIFORM AND
CONSTANT RATE**
10 Claims, 5 Drawing Figs.

[52] U.S. Cl...... **23/301R,**
23/273

[51] Int. Cl...... **B01j 17/04**

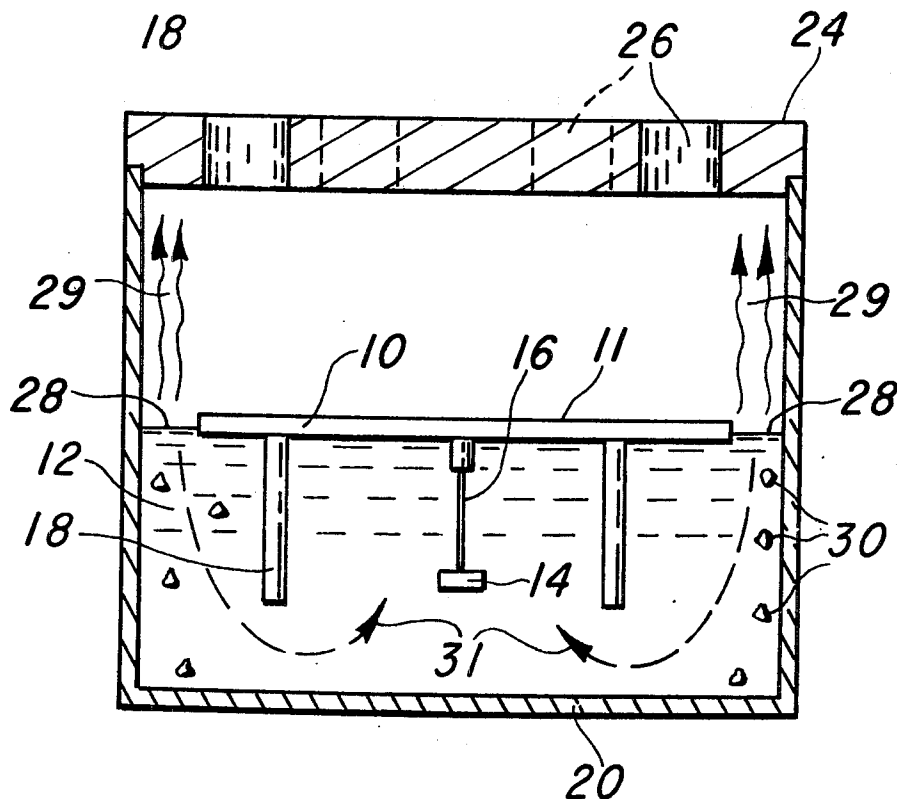
[50] Field of Search..... 23/301 SP,
301, 273 SD, 273, 85

[56] **References Cited**

UNITED STATES PATENTS

3,356,463	12/1967	Ballman et al.	23/301
-----------	---------	---------------------	--------

ABSTRACT: Disclosed is a method for growing crystals from solution wherein the rate of crystal growth is maintained uniform and constant. A holder for the crystal seed is constructed from material which has a specific gravity that causes it to float on the surface of the growth solution. The seed is suspended from the holder by a string or other suitable means and thereby positioned at a fixed distance below the surface where the solution is maintained at a constant saturation, thus insuring a uniform and constant growth rate of the crystal.



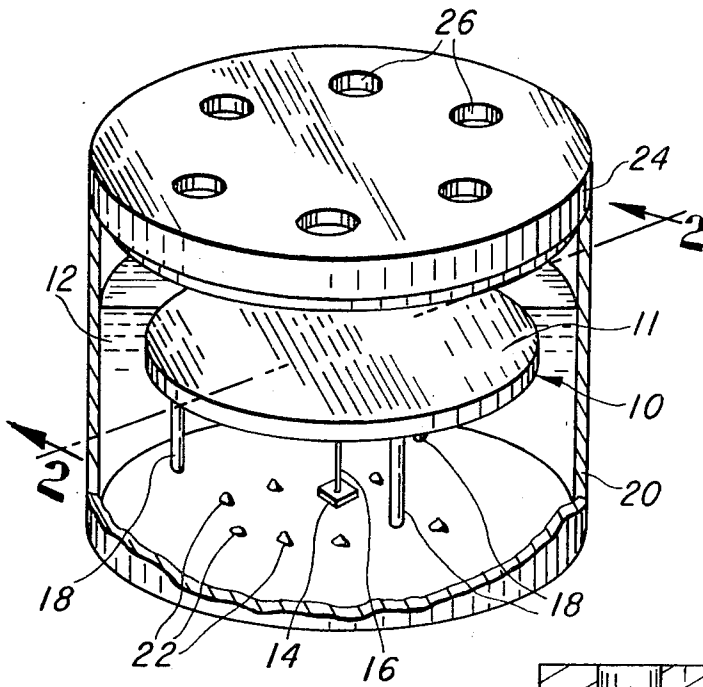


Fig. 1

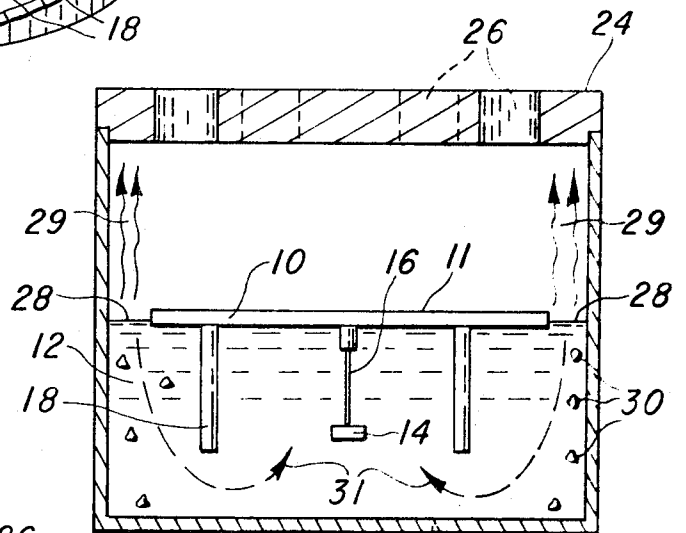


Fig. 2

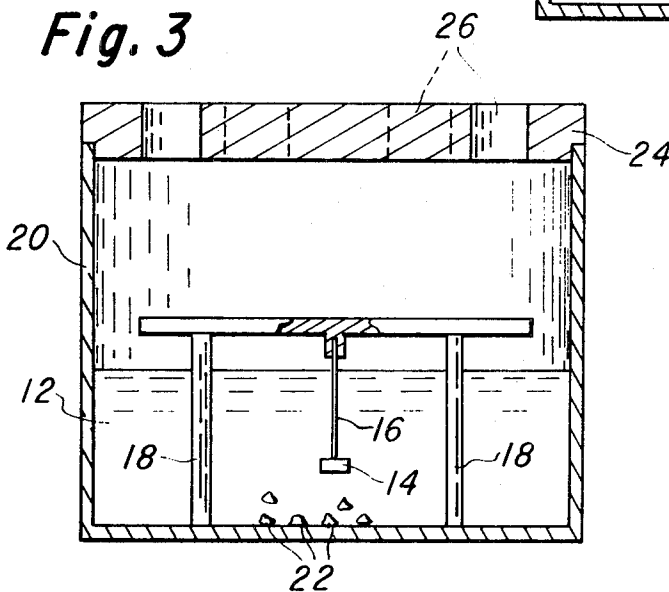


Fig. 3

INVENTOR
Sidney Glenn Parker

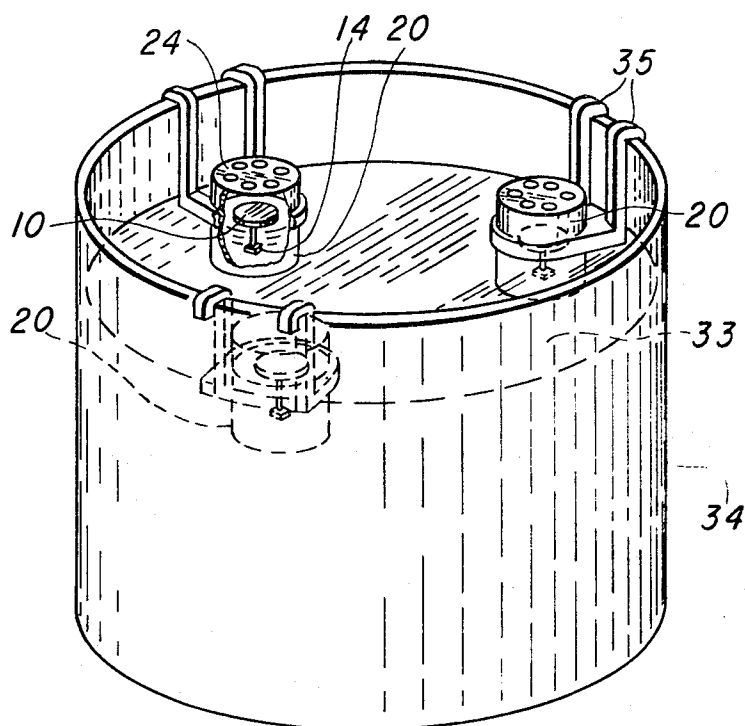


Fig. 4

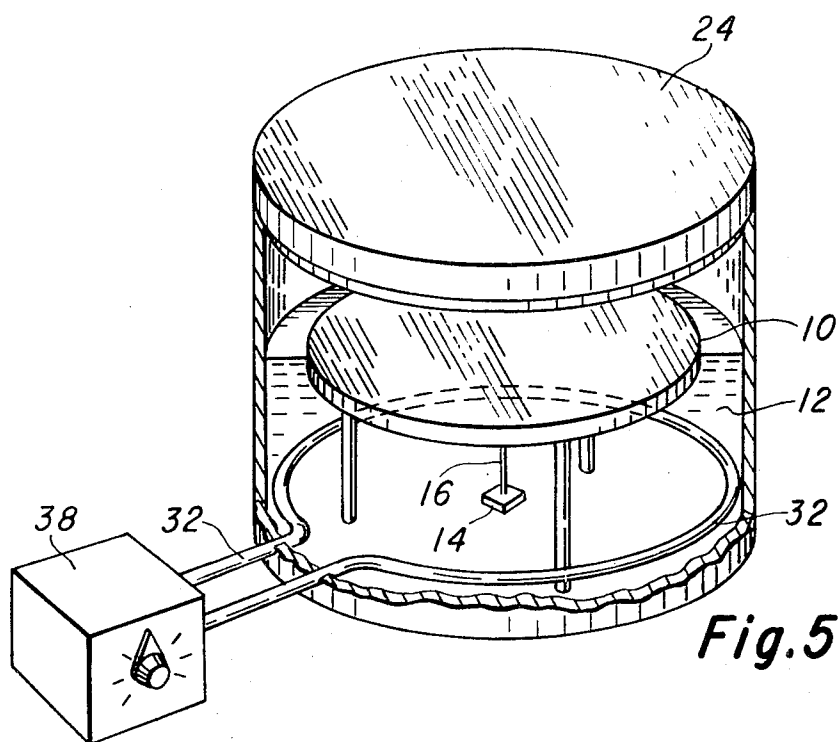


Fig. 5

GROWTH OF CRYSTALS AT A UNIFORM AND CONSTANT RATE

This invention relates to the growing of single crystals, and more particularly to a method of growing such crystals from a solution at a constant and uniform rate.

Many industries require substantially defectfree single crystals for a variety of applications. In particular, the utilization of such crystals in optics has recently gained wide attention. In the use of lasers, for example, defectfree single crystals like those of Iodic Acid (HIO_3), Lithium Iodate (LiIO_3) and Potassium Iodate (KIO_3) are particularly desirable because they possess excellent electro-optical characteristics.

According to the prior art, most single crystals are grown from a solution supersaturated with the material (solute) desired. That is, a saturated solution is caused to become supersaturated either by evaporation of a portion of the solvent or by lowering the temperature of the solution. A small single crystal of the solute itself, generally called a seed crystal, is then stationarily suspended in the solution. The "ordered" arrangement of the atoms of the seed crystal exert a "crystallographic attraction" upon the atoms of the solute and causes said atoms to deposit onto the seed crystal in the same ordered manner, thereby effecting growth of the single crystal.

Such crystals, however, are not easy to grow by prior techniques because of the difficulty of maintaining the solution at a steady concentration at the depth at which the seed crystal is immersed, because of a similar difficulty with respect to the temperature of the solution in the area thereof surrounding the seed crystal, and because of vibrations transmitted to the seed from within the container (as, for example, from stirring the solution) and from without the container, all of which, singly or in combination, result in the production of crystals having defects such as cracks, spurs, veils and polycrystalline structure. Such defects are detrimental to the electro-optic characteristics of the resulting crystals and therefore render them useless for many applications.

Accordingly, it is an object of the invention to row one or more single crystals from solution by a method which insures that the seed crystals therefor are maintained in a uniform concentration of solution, regardless of whether the concentration of solution is controlled by the evaporation of the solvent or by lowering the temperature of the solution.

It is a further object of the invention to shield the seed crystals from polycrystalline material formed on the surface and on the bottom of the solution.

It is an additional object of the invention to substantially insulate the seed crystals from the deleterious effects of vibrations.

Briefly, in accordance with the invention a seed holder, constructed to have a specific gravity less than that of the solution, is floated on the surface of the solution which is held within a suitable container, or tank, and a seed crystal, for example, is suspended from the holder by a string or other suitable means. As may be seen, the seed crystal is thereby maintained at a fixed and constant distance below the surface of the solution, even though the level thereof may substantially decrease during crystal growth. Thus positioned, the seed is continuously exposed to a solution having a substantially constant degree of saturation, which results in a constant and uniform rate of crystal growth.

The novel features believed to be characteristic of this invention are set forth in the appended claims. The invention itself, however, as well as other objects and advantages thereof, may best be understood by reference to the following detailed description of illustrative embodiments when read in conjunction with the accompanying drawings, in which identical designations in all of the figures refer to identical parts, and in which:

FIG. 1 is a perspective view of a typical solution container, or tank, utilized in connection with the present invention;

FIG. 2 is a side view along the line 2—2 of FIG. 1 diagrammatically depicting the seed holder floating on the surface of the solution;

FIG. 3 is similar to FIG. 2 but shows how the seed crystal is protected from polycrystalline material that forms on the bottom of the container.

FIG. 4 is a perspective view depicting how one or more of the containers of the kind illustrated in FIG. 1 may be immersed in a tank of liquid so as to maintain the temperature of the growth solution in each of the containers at a substantially constant level; and

FIG. 5 is a perspective view of a typical solution container, or tank, utilized in connection with the present invention, depicting apparatus suitable for varying the temperature of the solution.

Referring now to the drawings, and particularly to FIGS. 1—3, for the present, container 20, preferably round in contour, is comprised of any suitable material that is nonreactant with the solution 12 contained therein. It is preferred, however, that the container be transparent so that growth of the crystal within the solution may be visually observed. For most applications, glass or plastic is considered to be a suitable material for the container.

A seed holder 10 is comprised of a solid top 11, somewhat of smaller diameter than the container, from underneath which is suspended the seed crystal 14 by any suitable means 16 such as, for example, a soft plastic string or gold or platinum wire, each having a diameter of about 2 to 5 mils. The length of the string is not critical for the successful operation of the invention, the length being dependent solely upon the distance below the surface 28 of the solution 12 at which it is desired to suspend the seed 14. To the under surface of the top 11 is secured a suitable number of pedestals 18 of substantially equal lengths, or at least of such length as to keep the seed 14 above a predetermined depth of the solution when the pedestals engage the bottom of the container. As with the material of the container, the seed holder should be made of nonreactive material with respect to the composition of the growth solution. Thus by way of example, if the crystal to be grown is an iodic acid crystal (HIO_3) or a potassium iodate crystal (KIO_3) or a lithium iodate crystal (LiIO_3), the seed holder 10 should preferably be made of teflon, polypropylene plastic, polyethylene plastic, or any other material which is chemically nonreactive, respectively, to each of the growth solutions. In other words, the composition of the growth solution, whatever it may be, determines the parameters of the seed holder, including its specific gravity which should be less than that of the growth solution to enable it to float on the surface thereof.

Cover 24 encloses the container 20 and has a plurality of apertures 26 therewith, so that the rate of evaporation of the solvent from the solution 12 may be controlled and maintained uniform. It is understood that the apparatus shown in FIGS. 1—3 (and also that shown in FIG. 4 as later described) are for growing crystals by the evaporation of a portion of the solvent. However, if crystals are to be grown by lowering the temperature of the solution 12, the seed holder 10, floating on the solution 12 as shown, can still be advantageously utilized, as later explained in connection with the description of FIG. 5.

The operation of the present invention in an embodiment thereof for growing crystals by the evaporation of a portion of the solvent will now be described. The seed holder 10 floats on the surface of a substantial portion of the surface 28 of the solution 12. Evaporation of the solvent, therefore, must occur from the exposed surface 28, said evaporation being diagrammatically illustrated by arrows 29 in FIG. 2; hence, any polycrystalline material formed due to the increased saturation of the solution produced by the evaporation will necessarily occur in said exposed areas of the surface 28. The polycrystalline material thus formed is shown diagrammatically as particles 30 in FIG. 2, which either fall to the bottom of the container or adhere to the sides thereof. In no way, however, will the polycrystalline material come into contact with the crystal seed 14 and thereby cause nucleation sites thereon. Thus the seed holder 10 not only serves to hold the seed in suspension, but also serves to shield it.

Also shown diagrammatically in FIG. 2 is the effect of thermal convection, illustrated by arrows 31. As explained above, when the solution 12 evaporates from the exposed surface 28, the latter becomes cooler than the remainder of the solution, thereby establishing a temperature gradient from the surface (cooler) to the bottom (warmer) of the solution which correspondingly establishes a saturation gradient therethrough, with greater saturation at the surface and lesser saturation at the bottom. Since the seed 14 is suspended from the holder and is thereby positioned at a constant distance below the surface 28, it will be seen that the seed is continuously exposed to relatively the same saturation of the solution.

Again, the seed holder 10 floats upon the surface of solution 12 and is nowhere physically in contact with container 20. This feature, physically isolating the holder 10 from the container 20, serves to substantially insulate the seed crystal from vibrations generated external to the solution. For example, in the conventional process for growing crystals from solution the seed is physically attached to the container itself by a string attached to a pedestal secured to the container. Vibrations generated external to the solution are thereby provided with a ready path through the container to the attaching string and on to the crystal seed itself. In the present invention any such vibrations reaching the seed would first have to be transmitted through the liquid solution, and since a liquid is a relatively poor conductor of vibrations (as compared to a solid) the amplitude of such vibrations reaching the crystal seed would be greatly reduced, resulting in fewer, if any, crystal defects from internal stresses induced by the vibrations of the crystal.

It may be readily seen from FIG. 3 how the preferred embodiment of the present invention for growing crystals by evaporation of a portion of the solvent prevents the crystal 14 from coming into contact with the polycrystalline material, shown diagrammatically as 22, which forms on the bottom of the container 20. As previously stated, the pedestals 18, being secured to the underside of the seed holder 10, should be of such length so that when all the pedestals rest on the bottom of the container, the seed 14 is substantially above the polycrystalline material 22. It should be understood, however, that the successful operation of the present invention does not depend upon pedestals 18. The sole purpose of the pedestals is to prevent the seed crystal 14 from coming into contact with the bottom of the container 20 when the level of the solution 12 has been reduced to a predetermined level, it being obvious that if the container is preferably transparent, the distance of the crystal from the bottom of the container may be visually observed and the crystal withdrawn from the container when the desired distance is reached. Although the apparatus illustrated in FIGS. 1-3 shows only one crystal seed 14 suspended from the bottom of the seed holder 10, it should be recognized that any number of seed crystals, consistent with the size of the container and the appropriate dimension of the top 11 of the seed holder 10, could be suspended from under the seed holder.

In growing crystals by the evaporation of the solvent from the solution, it is necessary to maintain the solution at substantially a constant temperature. For many applications, in fact, the normal fluctuation of the room temperature may vary the temperature of the solution sufficiently to cause deleterious effects in crystal growth. It is common, therefore, to immerse the solution container 20 in a relatively large body of liquid, such as water, and thereby substantially isolate the growth solution from variations in ambient temperature.

FIG. 4 depicts utilization of such a liquid temperature bath with the present invention. In FIG. 4 is shown a plurality of solution containers 20, each partially immersed in a relatively large body of preferably room temperature water 33 contained in a tank 34. The solution containers, each with solution therein, are supported by suitable grippers 35 from the edge of the tank, each container 20 having its own seed holder 10 floating on the surface of the solution with a seed 14 suspended therefrom at the appropriate solution depth as previously described in connection with FIGS. 1-3.

FIG. 5 illustrates that embodiment of the invention by which crystals are grown by controlling the temperature of the solution. The apparatus is essentially the same as that illustrated in FIGS. 1-3 except that the cover 24 of the solution container has no apertures therein, thereby preventing any evaporation of the solvent. Within the container is suitable means 32 for varying the temperature of the solution 12. The temperature controlling means may comprise, for example, a heating element controlled by a variable power transformer 38.

Although the present invention has been described with a certain degree of particularity, it is understood that the present disclosures has been made by way of example and not by way of limitation and that the numerous changes in the details of construction and the combination of parts may be resorted to without departing from the spirit and the scope of the invention.

What is claimed is:

1. The process of growing crystals from solution at a uniform and constant rate of crystal growth, consisting of the steps of:
 - a. floating a seed holder having a specific gravity which is less than the solution on the surface of the solution;
 - b. suspending a single crystal seed from said holder whereby said seed is positioned at a constant distance below the surface of the solution; and
 - c. increasing the saturation of the solution to a supersaturated condition whereby the solute is crystallographically attracted to the seed and deposited thereon to effect a growth of the single crystal.
2. The method according to claim 1 wherein the step of increasing the saturation of the solution is by evaporation of a portion of the solvent.
3. The method according to claim 1 wherein the step of increasing the saturation of the solution is by lowering its temperature.
4. The method according to claim 1 wherein the seed holder includes pedestals affixed to its underside to prevent the seed from contacting polycrystalline material that becomes deposited on the bottom of the container.
5. The method of growing crystals according to claim 1 wherein the solution is HIO_3 .
6. The method of growing crystals according to claim 1 wherein the solution is KIO_3 .
7. The method of growing crystals according to claim 1 wherein the solution is LiIO_3 .
8. The method of growing crystals according to claim 4 wherein the seed holder is constructed of teflon.
9. The method of growing crystals according to claim 4 wherein the seed holder is constructed of polypropylene plastic.
10. The method of growing crystals according to claim 4 wherein the seed holder is constructed of polyethylene plastic.

* * * * *