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[54] **PERIODICALLY AND ALTERNATELY ACCELERATING AND DECELERATING ROTATION RATE OF A FEED CRYSTAL**

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[58] **Field of Search** ..... 23/301 SP, 273 SP

[56] **References Cited**

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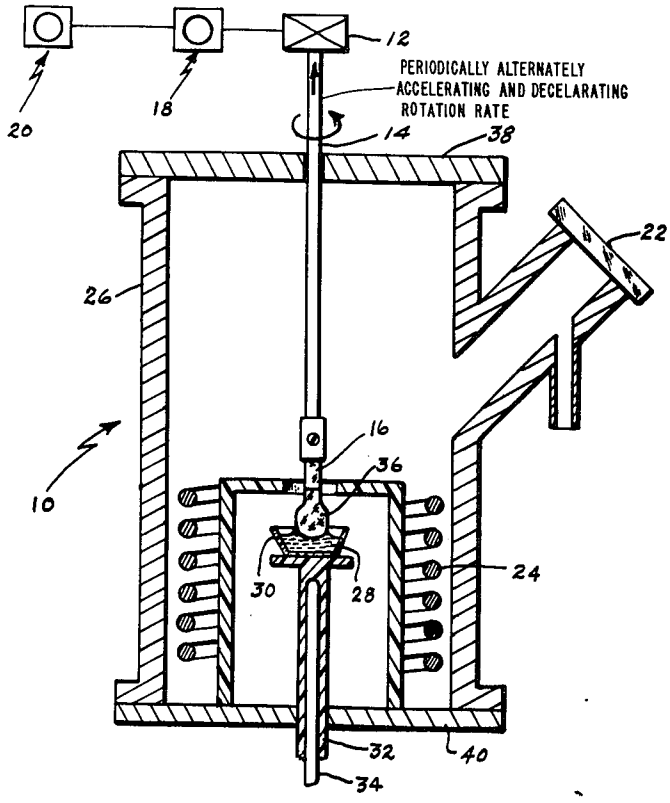
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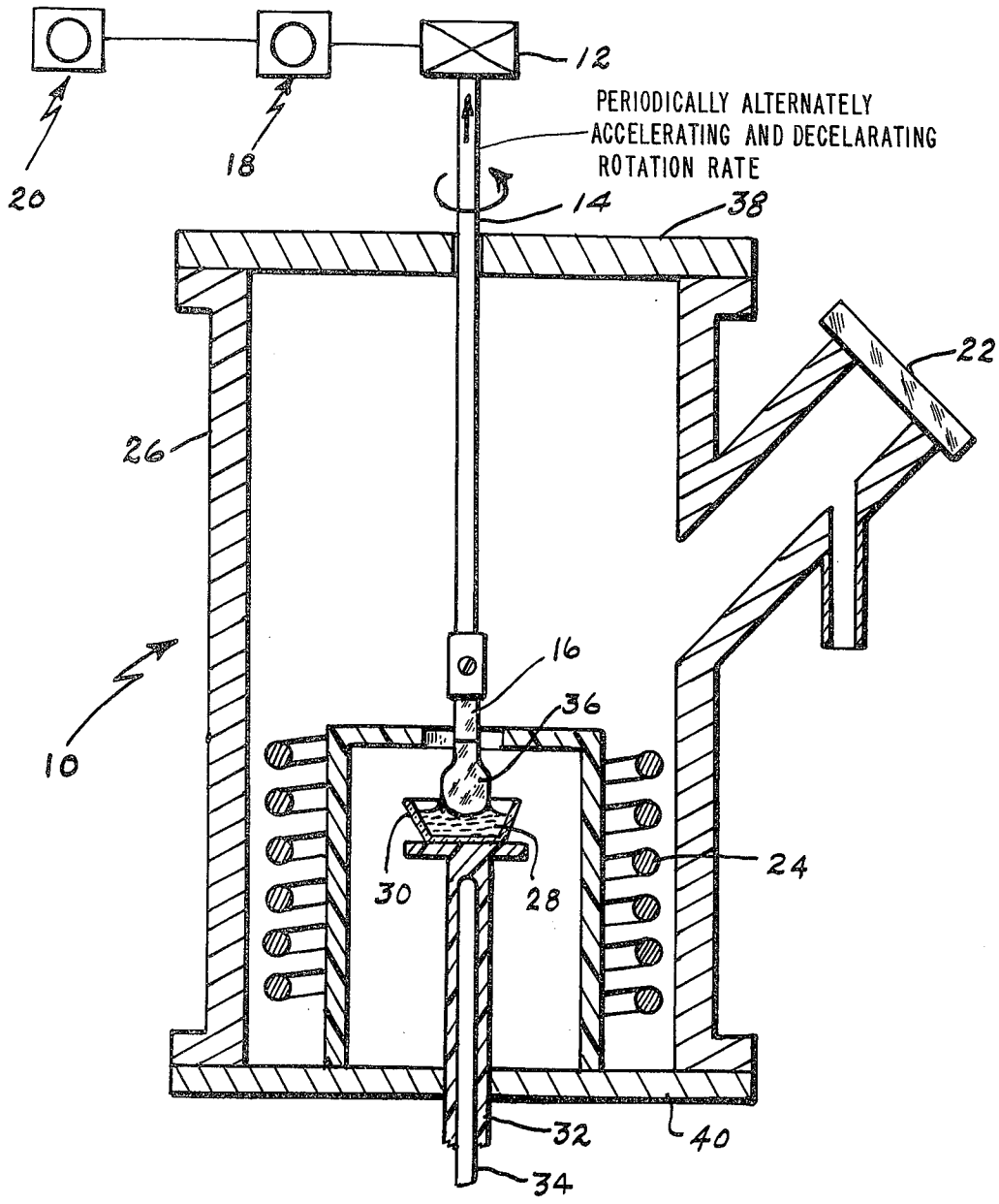
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[57] **ABSTRACT**

A method for growing a rod-like crystalline boule by placing a rotating seed crystal in contact with the surfaces of a molton solution of crystal growing materials, then withdrawing the seed crystal while simultaneously lowering the temperature of the solution and subjecting the rotating seed crystal to a periodic acceleration and deceleration of its rotation rate.

5 Claims, 1 Drawing Figure




12
PERIODICALLY ALTERNATELY
ACCELERATING AND DECELARATING
ROTATION RATE
20
18
14
38
22
26
16
36
10
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28
32
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PERIODICALLY AND ALTERNATELY ACCELERATING AND DECELERATING ROTATION RATE OF A FEED CRYSTAL

BACKGROUND OF THE INVENTION

This invention relates generally to a method for growing single crystal materials. More particularly, this invention concerns itself with an improved technique for growing crystalline boules which includes imparting a particular type of rotation to a seed crystal relative to a melt of crystalline growing material in such a manner that a crystalline boule of improved characteristics is produced.

Recent advances in the utilization of single crystals for various electronic applications has generated considerable research in the development of improved techniques for growing crystals having improved physical properties. A problem has arisen, however, in connection with the ultimate evaluation of the crystals physical characteristics. If a proper evaluation is to be made, then a crystal boule of excellent quality and of sufficient size for measurements must be produced. A number of methods are known for forming single crystals. The so-called Czochralski method, or crystal-pulling technique, has proven to be quite successful in producing rod-like crystal boules of considerable length. In this method, a seed crystal is placed on a rod which is lowered into a crucible containing a melt of crystal growing material. The seed crystal is placed in contact with the molten material and then slowly pulled from the melt. Since freezing occurs at the interface, growth occurs on the seed as it is withdrawn, resulting in the formation of a rod-like crystal boule. Another method, similar to Czochralski, is the Kryopoulos Technique. In this method, the seed, or a cooled rod, remains in contact with the molten crystal growing material and slow cooling causes crystallization to occur from the seed or rod into the melt. In these methods, the seed rod or the crucible is sometimes rotated as a modification of the basic technique. Also, these methods can be used under ambient conditions, vacuum or pressures up to 20 atmospheres as still further modifications. All have been employed at one time or another in attempts at providing large size crystalline boules of good quality.

However, the lack of homogeneity throughout the molten solution that comes in contact with the seed crystal has spawned the growth of boules of relatively poor quality although of sufficient size. The grown crystals do not exhibit a uniform stoichiometric compositional content throughout the crystal structure resulting in the formation of defects in the crystal body. The problem is especially acute when growing mixed single crystals having two or more chemical compounding constituents.

With this invention, however, it has been found that the problem of melt homogeneity that occurs when growing crystals with the well known crystal-pulling techniques can be drastically minimized by a modification that involves the periodic acceleration and deceleration of the rotation rate of the seed crystal at predetermined rates. The implementation of the modification of this invention provides crystal boules rod-like in character and of considerable length. The crystals show markedly better quality than crystals grown in accordance with previously known techniques.

SUMMARY OF THE INVENTION

In accordance with this invention, it has been found that rod-like crystalline boules of good quality and large size can be grown by a novel technique that imparts a periodic acceleration and a deceleration to the rotation rate of the rotating seed crystal utilized in the conventional crystal pulling methods for growing crystalline boules. The rotation of the seed crystal is accelerated and then decelerated at a constant rate. However, the acceleration cycle of seed rotation will vary depending upon the viscosity of the solution with thicker solutions requiring a lower rotation rate. The application of the acceleration affect promotes an even distribution of the crystal growing materials contained in the molten mixture. This reduces the problem of solution inhomogeneity near the growing crystal. The diffusion boundary is periodically shifted and the conditions favoring constitutional supercooling in the solution are drastically reduced. These two effects normally promote poor quality in growing crystals, but with the acceleration and deceleration concept of this invention, the two undesirable effects are overcome.

Accordingly, the primary object of this invention is to provide an improved method for growing high quality, large size, rodlike crystalline boules.

Another object of this invention is to impart a periodic rate of acceleration and deceleration to the rotation of the seed crystal utilized in the crystal pulling method for growing crystal boules.

Still another object of this invention is to provide an improved method for overcoming the problem of solution inhomogeneity that occurs when pulling crystals from a molten bath of crystal growing material.

Still other objects and advantages of the present invention will become apparent upon consideration of the following detailed description thereof when taken in conjunction with the accompanying drawing.

DESCRIPTION OF THE DRAWINGS

In the Drawings:

The FIGURE represents a schematic illustration of an apparatus suitable for use in carrying out the method of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In the method of this invention, rod-like crystalline boules of relatively large size and excellent quality are grown by a technique which involves the step of periodically accelerating and decelerating the rotation rate of a rotating seed crystal at a constant rate for a predetermined period of time. The well known crystal pulling technique for growing single crystals includes the step of rotating a seed crystal as it is slowly withdrawn from a molten bath of crystal growing material. This method is often referred to as the Czochralski method and, in general, involves the steps of placing a rotating seed crystal in contact with a molten solution of a crystal growing material. The seed crystal is slowly withdrawn from the molten compound. Freezing occurs at the interface resulting in the formation of a rod-like crystalline boule on the rotating seed crystal as it is withdrawn. The seed crystal is rotated at a specific rate over a predetermined time depending upon the particular material being grown, melt temperature and other well known growth variables.

In this invention, however, it has been unexpectdely found that improved crystalline boules, both as to quality and size can be grown if the rotation rate of the said crystal is periodically accelerated and then decelerated. The periods of accelerating and decelerating the rotation rate occurs at a constant rate over a predetermined time. The acceleration cycle is varied only with respect to the viscosity of the solution used for growing the crystal. For a solution with a viscosity of 40 poise, the seed crystal acceleration cycle is: 0 rpm to 50 rpm to 0 rpm with a cycle time of 1 minute. For solutions with a viscosity greater than **40** poise, the maximum rpm must be less than 50. For solutions with a viscosity of less than 40 poise, the maximum rpm must be greater than 50.

Attention is now directed to the FIGURE in the drawing which shows, in schematic form, a conventional Czochralski type vertical pull crystal growing apparatus. The apparatus is suitable for carrying out the practice of this invention and comprises, in general, a crystal growing furnace **10,** a motor **12** for rotating and pulling a shaft **14** which in turn is connected to a seed crystal **16.** The acceleration and deceleration of the rotating crystal is accomplished by means of a conventional motor speed controller **18** and a variable slow speed motor. The elements **18** and **20** are each connected to a suitable source of electric power, not shown. The furnace **10** also includes a viewing port **22,** a heating element **24** for melting the crystal growing compound, and a water-cooled chamber **26** for cooling the growing crystal **36** as it is withdrawn from the molten crystal growing material **28.** The melt **28** is positioned within a crucible **30** located on top of a crucible support **32.** A temperature sensor **34** is positioned adjacent to the crucible in order to control the temperature of the melt **28.** Suitable top and bottom covers are shown respectively at **38** and **40** in order to provide a closed and controlled atmosphere for the growing process.

The novel procedure for growing crystals in accordance with the modified crystal pulling technique of this invention initially involves growing C-axis oriented needle-like crystals for use as a seed. These are grown by cooling a solution of crystal growing material in the presence of platinum wire which is attached to a seed rod. In carrying out the practice of the invention, a seed crystal **16** is placed on the end of a shaft or seed rod **14** and dipped into the surface of a molten solution of crystal growing material **28** which has been previously heated by coils **24** to a temperature above the melting point of the crystal growing solution. The melt **28** is then slowly cooled at a programmed rate while the seed rod is slowly withdrawn and rotated at the predetermined rate. The rotation rate is periodically accelerated and then decelerated at a constant rate for a fixed period of time. The acceleration rate varies with the viscosity of the melt **28.** Solutions having a viscosity of 40 poise requires a rotating cycle of 0 rpm to 50 rpm to 0 rpm with a cycle time of 1 minute. The rotating cycle of acceleration and deacceleration is maintained at the predetermined rate until crystal growth is completed. For solutions having a viscosity greater than 40 poise, the maximum rpm must be less than 50 while for solutions with a viscosity of less than 40 poise, the maximum rpm must be greater than 50.

To further illustrate a specific embodiment of the invention reference is made to the following description of the formation of tetragonal single crystals of germanuim dioxide. A mixture of electronic grade germanuim dioxide with a reagent grade alkali oxide, such as lithium, sodium or potassium, as the solvent were dry mixed for 15 hours and then placed in a platnuim crucible in a Czochalski type apparatus such as shown in the drawing. The mix contained 90.36 molar percent G_eO_2 with Li_2O; 92.30 molar percent G_eO_2 with Na_2O and 93.96 molar percent with K_2O.

The mixture with Li_2O as the solvent was heated to 1,200°C and held at that temperature for one hour for addition mixing. A seed crystal was placed in contact with the surface of the melt and rotated while the melt temperature was slowly lowered at a programmed rate of 2°C per hour. The seed crystal rotation was periodically accelerated and decelerated at a constant rate of from zero rpm to 30 rpm to 0 rpm for an acceleration cycle period of 1 minute. This periodic change in the rate of rotation was maintained until a crystal of sufficient length was grown. All crystallization occurred on the seed as the temperature of the bath was lowered between approximately 1,050°C to 975°C. As the solution was about to freeze at its eutectic point, the crystal was pulled out of the melt. The crystal was then cooled at about 200°C per hour to room temperature. A pull rate of 0.50 mm per hour permitted the growth of tetragonal germanium dioxide crystals of about 3 mm times 10 mm in size. The crystals were grown on the 001 plane and were single as shown by its Laue pattern following seed orientation.

The method of this invention is clearly applicable to other materials which can be formed into rod-like single crystals or where a seed crystal can be rotated as it comes in contact with a molten solution of crystal growing material. It is to be understood, also, that the method of this invention may be altered or modified in any manner which suggests itself to those skilled in the art and that all such modification as fall within the scope of the appended claims is intended to be included herein.

What is claimed is:

1. In a system for growing single crystalline boules which comprises the steps of placing a seed crystal in contact with the surface of a molten solution of crystal growing material, lowering the temperature of the molten solution at a programmed rate to a temperature sufficient to effect the formation of a rod-like crystalline boule on said seed crystal while simultaneously rotating and withdrawing said seed crystal during said lowering of said temperature, and cooling said formed crystalline boules to room temperature, the improvement which comprises periodically altering the rotation rate of said rotating seed crystal by alternately accelerating and decelerating said rate of rotation at a constant rate for a predetermined period of time.

2. A method in accordance with claim **1** wherein said rate of rotation must be less than 50 revolutions per minute when the viscosity of said molten solution is greater than 40 poise.

3. A method in accordance with claim **1** wherein rate of rotation must be greater than 50 revolutions per minute when the viscosity of said molten solution is less than 40 poise.

4. A method in accordance with claim **1** wherein the rate of rotation of said rotating seed crystal is accelerated from 0 to 50 revolutions per minute and then decelerated from 50 to 0 revolutions per minute at a constant rate for a period of about 1 minute.

5. A method in accordance with claim 1 wherein said temperature of said molten solution is lowered from 1,200°C to 975°C at a programmed rate of 2°C per hour; said rate of rotation is periodically altered by accelerating from 0 to 30 revolutions per minute and decelerating from 30 to 0 revolutions per minute at a constant rate for a period of one minute and said rotating seed crystal is withdrawn from said molten solution at a rate of 0.50 mm per hour.

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