

[54] **METHOD FOR PRODUCING CRYSTAL BOULES WITH EXTENSIVE FLAT, PARALLEL FACETS**

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[51] Int. Cl. **B01j 17/18**

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

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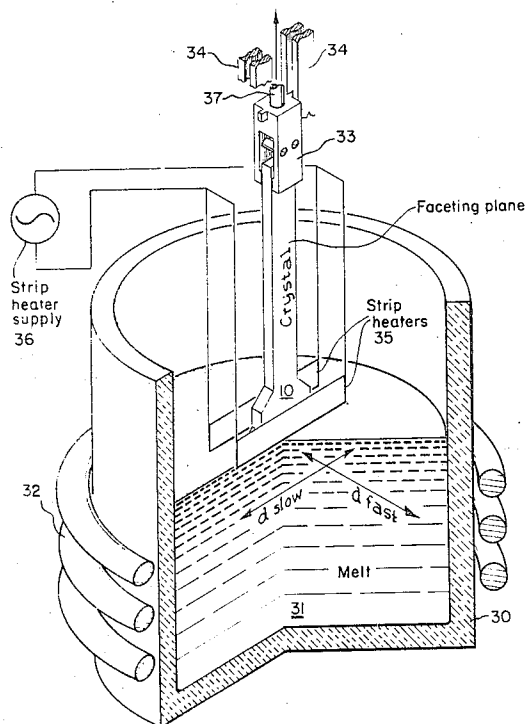
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[57] **ABSTRACT**

A particular symmetric anisotropic temperature distribution is established at the crystal-melt interface and the seed crystal is pulled from the melt to produce a crystal boule. The seed crystal is oriented in a specific crystallographic direction and is prevented from rotation with respect to the temperature symmetry axes while being withdrawn from the melt. The temperature distribution is such that the temperature varies slowly with varying distance from the center of the crystal boule along a first axis defining the crystal boule width, and varies rapidly with distance along a second axis perpendicular to the first and which defines the crystal boule thickness. The maintenance of the particular anisotropic temperature distribution at the crystal-melt interface produces a single crystal boule with a pair of extensive flat, parallel facets that are microscopically smooth.

6 Claims, 6 Drawing Figures



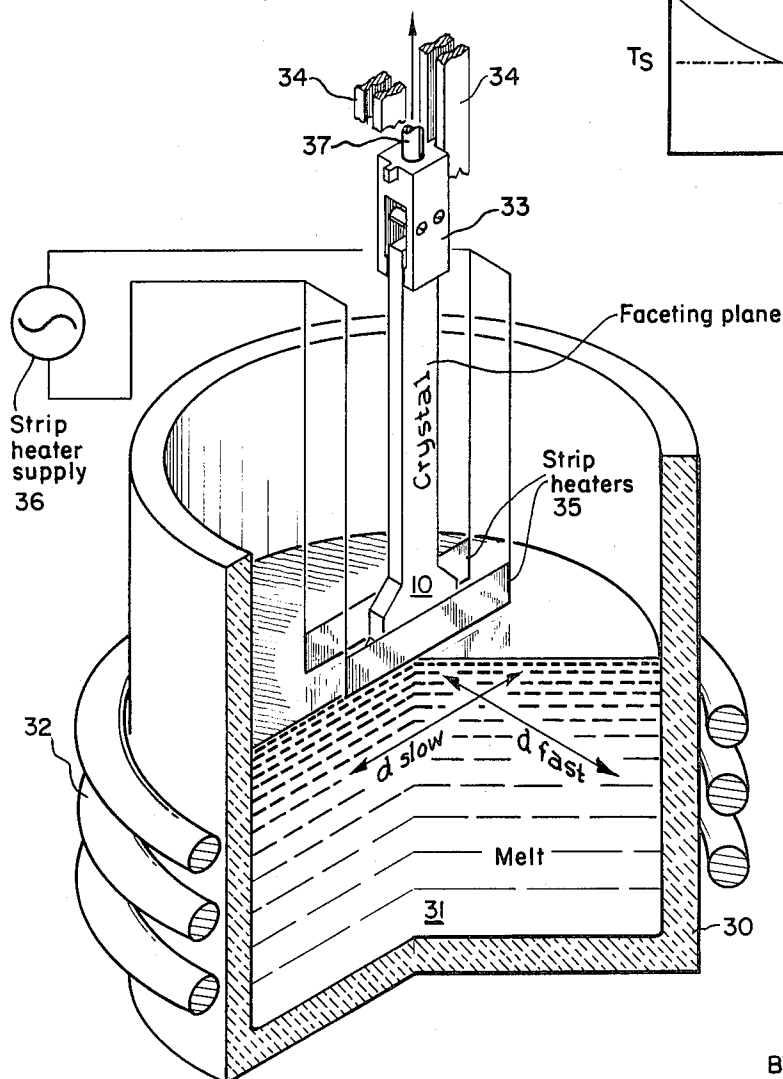
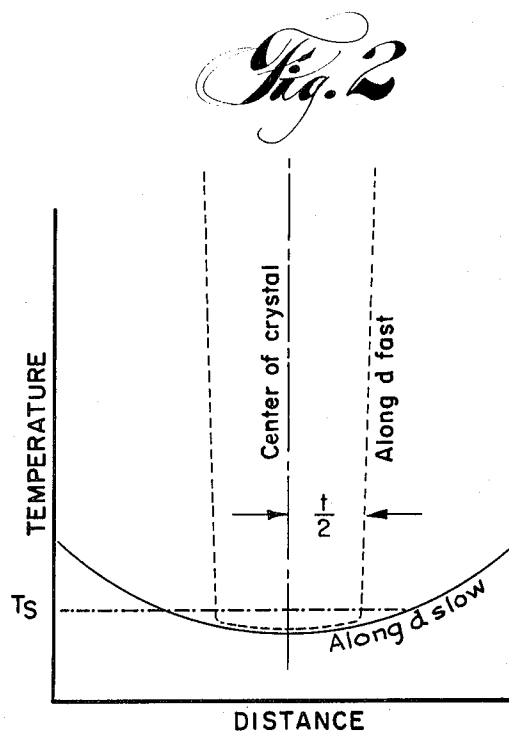
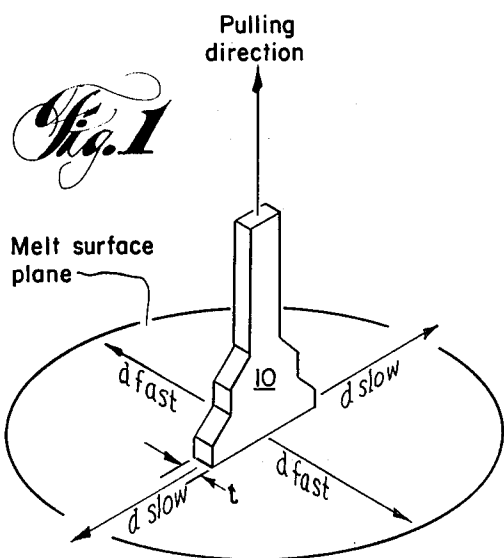


Fig. 3a

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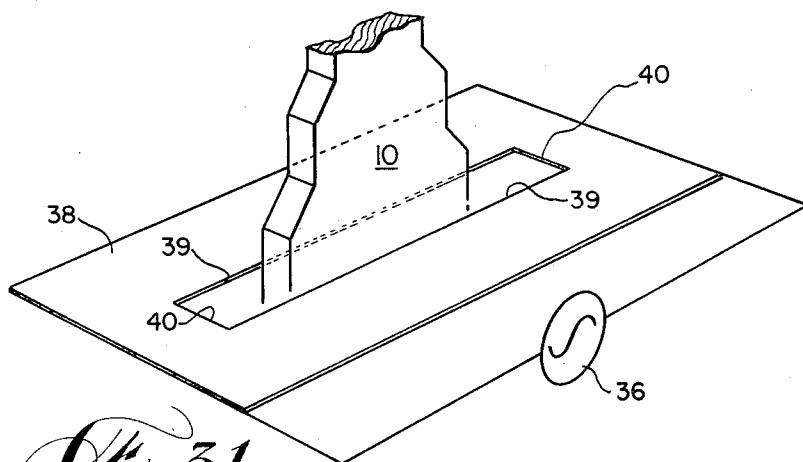


Fig. 3b

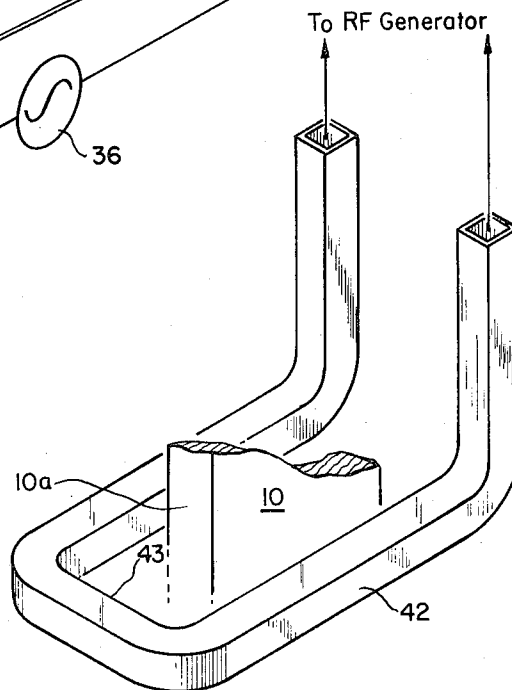


Fig. 3c

SOME CRYSTAL ORIENTATIONS FOR THREE CUBIC CRYSTALS				
Crystal	Normal to principal faceting plane	Direction along d fast	Direction along d slow	Pulling direction
$\text{Bi}_{12}\text{GeO}_{20}$	$[100]$	$[100]$	$[011]$	$[0\bar{1}1]$
$\text{Y}_3\text{Al}_5\text{O}_{12}$	$[\bar{2}11]$	$[\bar{2}11]$	$[111]$	$[0\bar{1}1]$
Si	$[111]$	$[111]$	$[01\bar{1}]$	$[\bar{2}11]$

Fig. 4

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METHOD FOR PRODUCING CRYSTAL BOULES WITH EXTENSIVE FLAT, PARALLEL FACETS

My invention relates to a method for producing crystal boules having flat, microscopically smooth and parallel facets, and in particular, to a method employing the step of establishing a particular symmetric anisotropic temperature distribution at the crystal-melt interface.

In the growth of crystals by the Czochralski, pedestal or floating zone methods, extensive facets are observed on the surfaces of the grown crystal boules. Examples of such faceting are [111] facets in web dendrite silicon, planar facets in calcium pyroniobate, and planar facets in $\text{Bi}_{12}\text{GeO}_{20}$ pulled in [100] direction. Temperature fluctuations at the crystal-melt interface can be made small by proper system design but cannot be eliminated completely. Such temperature fluctuations cause small growth steps to form on the facet surfaces thereby preventing the fabrication directly from crystal boules of crystal devices which require microscopically smooth, parallel surfaces.

Several recent U.S. Pat. Nos. such as 3,494,804 to C.W. Hanks et al, are concerned with related problems of crystal growth and propose particular solutions. However, the Hanks et al patent relates to the production of a single crystal having a circular cross section and therefore merely requires a temperature distribution at the crystal-melt interface that is substantially equal around such interface. Such temperature distribution is not capable of producing a single crystal having microscopically smooth, flat, parallel facets.

Therefore, the principal object of my invention is to provide a method for producing crystal boules having extensive, flat, parallel facets that are microscopically smooth.

Another object of my invention is to provide such method by establishing a particular symmetric anisotropic temperature distribution at the crystal-melt interface whereby the temperature varies at a slow rate with increasing distance from the center of the crystal boule along a first axis and varies rapidly along a second axis which is perpendicular to the first.

A further object of my invention is to provide a device made from a single crystal having flat, microscopically smooth surfaces free from mechanical damage and in which two of such surfaces are accurately parallel.

Briefly summarized, my invention is a method for producing single crystals having surfaces that are flat, microscopically smooth, free from mechanical damage and having two surfaces accurately parallel. The crystals having such desired characteristics are cut from crystal boules grown in the following manner. A melt of the crystalline material is formed, and a seed crystal, oriented in a specific crystallographic direction, is dipped into the melt to form a crystal-melt interface. An auxiliary heating means is used to establish a particular symmetric anisotropic temperature distribution at the crystal-melt interface such that the temperature varies slowly with varying distance from the center of the crystal along a first axis defining the crystal width, and varies rapidly with distance along a second axis perpendicular to the first and which defines the crystal thickness. The seed crystal when withdrawn from the melt is prevented from rotating with respect to the symmetry axes of the anisotropic temperature distribution

and produces a single crystal boule with a pair of extensive flat, microscopically smooth, parallel facets from which a crystal having accurately parallel surfaces may be cut.

The features of my invention which I desire to protect herein are pointed out with particularity in the appended claims. The invention itself, however, both as to its organization and method of operation, together with further objects and advantages thereof, may best be understood by reference to the following description taken in connection with the accompanying drawings wherein:

FIG. 1 is a perspective view of a crystal boule produced in accordance with my invention and illustrates a particular symmetric anisotropic temperature distribution at the crystal-melt interface which is a feature of my invention;

FIG. 2 is a graphical representation of the crystal boule growth with temperature variation at the crystal-melt interface.

FIG. 3a is a perspective view, partly in section, of a first embodiment of an apparatus adapted for producing the crystal boule in accordance with my invention;

FIGS. 3b and 3c are enlarged views of two additional embodiments of the auxiliary heating means which may be utilized in the apparatus in FIG. 3a, and

FIG. 4 is a table indicating crystal orientations for three cubic crystals grown in accordance with my invention.

A conventional method for producing single crystals, or more correctly, single crystal boules (due to the generally pear-shaped mass formed by this method), consists of dipping a single seed crystal into a melt of the crystalline material to thereby form an interface between the seed and melt. The seed crystal is then pulled or otherwise withdrawn from the melt at a predetermined rate sufficiently slow to cause the melt material to solidify on the seed crystal continuously as the seed is withdrawn and thereby produce the crystal boule. Such crystal boule is of a generally circular cross section. My invention provides a crystal boule at rectangular cross section, or at least having two parallel sides.

Referring now to FIG. 1, there is shown the growth of a single crystal boule 10 from the seed crystal which is the rectangular upper portion of the crystal boule. The top surface of the melt material is designated as the "melt surface plane" and the intersection thereof with the bottom surface of the crystal boule is the crystal-melt interface, it being recognized that such interface is not a truly planar surface due to meniscus formed around the boule during the crystal boule growing operation. The seed crystal is withdrawn at the above-described sufficiently slow rate in a direction normal to the melt surface plane as indicated by the arrow designated "pulling direction" directed vertically upward.

Temperature fluctuations inherently occur at the crystal-melt interface and along the melt surface plane even though the melt temperature is controlled, due to many factors including (1) changes in the line voltage supplied to the heating means which maintains the melt material in its liquid state and (2) thermal convection currents which are developed in the crucible or other device containing the melt. These temperature fluctuations would generally cause undesirable small growth steps to form on the facet surfaces of faceting type crystals.

tals thereby preventing the growth of crystal boules having extensive microscopically smooth, parallel facets. The essence of my invention is the establishment of a particular symmetric anisotropic temperature distribution at the crystal-melt interface and along the melt surface plane immediately adjacent thereto. The particular temperature distribution is such that the temperature varies slowly with varying distance from the center of the crystal boule along a first axis designated "d slow" which defines the crystal boule width and varies rapidly with varying distance beyond one half the boule thickness dimension (t) along a second axis designated "d fast" which is perpendicular to the first axis and which defines the crystal boule thickness. For distances along the second axis less than $t/2$, the temperature varies at substantially the same slow rate as along the "d slow" axis. In particular, temperature increases slowly with increasing distance from the boule center along the "d slow" axis, and increases rapidly along the "d fast" axis beyond distance $t/2$.

The temperature variation with varying distance from the center of the crystal boule is indicated graphically in FIG. 2 wherein the temperature vs. distance variation along the "d slow" axis is a solid line, and along the "d fast" axis is a dashed line. Thus, it can be seen from the FIG. 2 graph that the crystal boule growth along the "d slow" axis increases rapidly with decreased temperature at the crystal-melt interface, and increases very slowly (near zero rate) along the "d fast" axis beyond distance $t/2$. As a result, any formation of small growth steps due to temperature fluctuations at the crystal-melt interface will preferentially occur along the "d slow" axis rather than along the "d fast" axis since the solidification (melting) temperature T_s for the particular crystalline material is somewhat above the value corresponding to distance $t/2$ from the boule center. Orientation of the seed crystal is in a particular crystallographic direction such that the "d fast" axis is normal to the naturally faceting surfaces of the specific seed crystal employed, and prevention of rotation of the seed crystal upon its gradual withdrawal from the melt assures the production of a crystal boule having a pair of facets normal to the "d fast" axis and which are microscopically smooth due to the lack of any growth steps thereon.

Referring now to FIG. 3a, there is shown a first embodiment of an apparatus adapted for growing a crystal boule in accordance with my invention. A crucible 30, or other suitable container for the material to be grown into the crystal boule, is filled to a prescribed level with such material 31 which is thence heated in any conventional manner to obtain a liquid state or melt of the material 31. The prescribed level of the molten material is maintained in container 30 by adding further material as such level tends to decrease upon the crystal boule undergoing its growth formation. Suitable heating means for crucible 30 are an induction heating coil 32 disposed about the crucible and radiant heating from a resistance furnace as two examples. Crucible 30 is initially heated to a high temperature for changing the state of the crystalline material from solid to liquid (molten), and the temperature is then reduced to maintain the average temperature of the molten material 31 somewhat above the melting point by means of a suitable control circuit (not shown) associated with the heating means 32. However, as mentioned above, inherent small temperature fluctuations still occur in the

molten material, and in particular at the top surface thereof at which occurs the crystal-melt interface.

The seed crystal 10 is held in a suitable clamping means 33 connected to a conventional crystal pulling mechanism 37 for lowering the seed crystal for the initial dip into the melt to create the crystal-melt interface and thence for raising the seed crystal in the pulling direction indicated in FIG. 1. A suitable guide means 34 prevents rotation of the seed crystal and growing crystal boule as it is being withdrawn from the melt. Obviously, many other types of clamping means and mechanisms for movement of the clamping means as well as other types of rotation prevention means may be utilized. Spaced slightly above the top surface of the melt is an auxiliary heating means 35 for establishing the desired symmetric anisotropic temperature distribution at the crystal-melt interface. The first embodiment of such auxiliary heating means as illustrated in FIG. 3a is a pair of strip heaters 35 comprising rectangular electrically conductive equal resistance, strip elements of length substantially greater than the maximum anticipated width of the crystal boule to be grown. Electrical conductors connected at opposite ends of the two strip heaters and to a controlled source of electric power 36 provide the desired electric current through the strip heaters to thereby establish a particular temperature distribution at the crystal-melt interface. Strip heaters 35 are disposed parallel to each other, parallel to the melt surface, and parallel to the faceting planes of the crystal boule. The strip heaters are spaced slightly from the faceting planes, such that they limit the crystal boule thickness dimension to substantially the value " t ." Thus, it can be appreciated that a symmetric anisotropic temperature distribution is created at the crystal-melt interface and comprises a substantially equal high temperature zone along the two parallel faceting planes of the crystal boule and a substantially lower temperature zone along the two nonfaceting sides which determine the crystal boule width. Due to the heat generated by strip heaters 35, the temperatures on all four sides of the crystal boule are somewhat higher than the average temperature of the melt. The crystal boule increases in its length dimension (pulling direction) as the seed crystal is drawn upward from the melt, and the heat of fusion involved in this growth reduces the crystal-melt interface temperature to a stabilized value along the steep portion of the temperature-distance curve illustrated in FIG. 2. The inherent temperature fluctuations at the crystal-melt interface cause the rate of solidification to vary with a resulting change in the crystal boule width dimension. Thus, as the crystal-melt interface temperature increases (or decreases), the crystal boule dimension decreases (or increases) along the "d slow" axis while remaining substantially constant along the "d fast" axis due to the proximity of the strip heaters and the steepness of the temperature-distance curve along which this temperature variation occurs. Growth of the crystal boule along its longitudinal dimension thus also includes growth, or at least variation in dimension, along the "d slow" axis in response to the inherent temperature fluctuations, but no variation in dimension along the "d fast" axis. Therefore, the crystal boule produced as a result of maintaining the desired crystal orientation and the symmetric anisotropic temperature distribution of the crystal-melt interface has a pair of surfaces (faceting planes) which are microscopically smooth due to the

absence of growth steps thereon. These microscopically smooth surfaces are equivalent to that produced after growing crystals by conventional techniques and utilizing a subsequent polishing operation, but without the mechanical damage often developed in the polishing step. The faceting planes are flat, and parallel due to the orientation of the seed crystal in the particular crystallographic direction selected for the specific material utilized. The temperature fluctuation is damped by melting or solidification in the "d slow" direction which does not cause the formation of growth steps on the facet surfaces.

FIG. 3b illustrates a second embodiment of an auxiliary heating means for establishing a symmetric anisotropic temperature distribution at the crystal-melt interface. The second embodiment is a slotted plate 38 fabricated of an electrically conductive material such as the strip heaters in the FIG. 3a embodiment, which may be fabricated of copper as one example. The slotted plate is connected to a suitable controlled power supply 36 and is disposed slightly above the melt surface as in the case of the strip heaters. Plate 38 is parallel to the melt surface, and the seed crystal 10 is pulled upward through the slot in the plate in the same manner as the seed crystal is pulled upward between the strip heaters in the first embodiment. The slot in plate 38 is rectangular and of dimensions such that the faceting planes of the crystal boule are slightly spaced from the long sides 39 of the slot which are parallel to the "d slow" axis whereas the nonfaceting sides of the crystal boule are substantially spaced from the short ends 40 of the rectangular slot. Thus, an equally higher temperature zone is developed along the faceting plane sides of the crystal-melt interface and a lower temperature zone along the nonfaceting sides thereof, as in the case of the first embodiment.

Finally, FIG. 3c illustrates a third embodiment of an auxiliary heating means for establishing the symmetric anisotropic temperature distribution at the crystal-melt interface. This third embodiment is an electrically conductive hairpin coil 42 having its ends connected to a suitable radio frequency (RF) generator. The hairpin coil 42 is a U-shaped member bent upward near its ends for connection to the radio frequency generator. Coil 42 may be of many shapes in cross section including square, rectangular and circular as three examples. This third embodiment is especially well adapted for the growth of crystal boules with a resistivity of the order of or less than 0.01 ohm-cm. near their melting point. Coil 42 may be hollow and water cooled whereby the crystal boule dimension along the "d fast" axis is controlled by the fact that heat from radio frequency (electromagnetic) coupling to the crystal boule increases rapidly as the faceting sides of the crystal boule approach coil 42. Other cooling means may also be employed with coil 42. Coil 42 may also be operated uncooled in which case heat transferred to the crystal boule results from radiation, thermal convection and electromagnetic induction. Again as in the case of the first two embodiments, the long sides of the coil 42 are parallel to the faceting planes of the crystal boule and slightly spaced therefrom whereas the bottom portion 43 of the U-shaped member is substantially spaced from the nonfaceting side 10a of the crystal boule. Obviously, many other types of heating means may be employed for establishing the desired symmetric anisotropic temperature distribution at the crystal-melt in-

terface. Further examples of these heating means are the use of (1) unheated reflectors in the place of the strip heaters 35 of FIG. 3a and (2) heat transport from a gas by maintaining a greater flow of gas through heat porous plates located in the position of the strip heaters.

FIG. 4 is a table of three representative crystals indicating seed crystal (and crystal boule) orientations utilized for growing the single crystal boules with extensive flat, parallel facets that are microscopically smooth in accordance with my invention. In particular, three cubic type crystals are listed, namely, $\text{Bi}_{12}\text{GeO}_{20}$, $\text{Y}_2\text{Al}_5\text{O}_{12}$ and Si. It should be understood that the crystallographic directions and faceting planes are characteristic of the particular crystal utilized. The tendency to facet in some cases can be altered somewhat by the presence of impurities in the melt, however, the normal to the faceting planes is always along the "d fast" axis. In the examples indicated in FIG. 4, the nonfaceting or weakly faceted direction is along the "d slow" axis.

As an example of the state of the art techniques in growing crystals by pulling a seed crystal from a melt, a crystal of 1 centimeter diameter generally develops lateral deviations in the order of 0.05 millimeter in the presence of a carefully controlled temperature of the melt. This 0.05 millimeter deviation is far from approaching microscopically smooth surfaces such as may be obtained by utilizing polishing operations to obtain a desired smoothness. Smooth, flat, parallel surfaces for devices such as an optically pumped crystal laser or electron pumped semiconductor laser made from single crystals have been produced in the past by either polishing or cleaving the crystals. In the case of polishing, very smooth and flat surfaces have been produced, but alignment of the surface with a crystallographic direction and attainment of surface parallelism has been limited by the optical and X-ray measurements available, and these surfaces are generally mechanically damaged in the polishing process. In the case of cleaving, the surfaces are accurately aligned with crystallographic directions that are accurately parallel when two cleaved surfaces are used, however, the surface area which can be cleaved without surface steps is limited, and some crystals cannot readily be cleaved. My invention results in the production of single crystal boules which have been grown in a manner to produce natural facets oriented in a specific crystallographic direction such that the facet comprises a crystallographic plane of the particular crystal thereby resulting in an accurately parallel pair of facet surfaces. The symmetric anisotropic temperature distribution at the crystal-melt interface permits the production of such accurately parallel facet crystal boules with the facets having microscopically smooth surfaces requiring no additional polishing process. The single crystal devices are obtained by cutting from the grown crystal boule a portion thereof and utilizing such cut portion directly as the device. As one example, a portion of a $\text{Bi}_{12}\text{GeO}_{20}$ crystal boule operated satisfactorily as a reverberating acoustic delay line at a frequency of 500 megahertz.

It is apparent from the foregoing that my invention attains the objectives set forth in that it provides a method for producing crystal boules having extensive flat, parallel facets that are microscopically smooth. An essential step in the method includes establishing a particular symmetric anisotropic temperature distribution

at the crystal-melt interface such that the crystal dimensional variation is induced to develop at a very slow (approaching zero) rate in the normal direction to the faceting planes while varying at a fast rate in the direction perpendicular thereto in response to inherent small temperature fluctuations at the crystal-melt interface. Single crystals may then be cut from the grown crystal boules and utilized in any of a number of devices such as optically pumped crystal lasers and electron pumped semiconductor lasers which require two surfaces that are flat, microscopically smooth, free from mechanical damage and accurately parallel, and may also be utilized in devices requiring only one damage-free microscopically smooth, planar surface such as acoustic surface wave devices (filters and delay lines).

Having described three embodiments of auxiliary heating means suitable for establishing the necessary symmetric anisotropic temperature distribution at the crystal-melt interface, it is believed obvious that other suitable heating means may also be employed to establish the necessary high equal temperature region adjacent the faceting planes of the crystal and the lower temperature zone along the nonfaceting surfaces of the crystal at the crystal-melt interface. It is, therefore, to be understood that changes may be made in the particular embodiments of my invention described which are within the full intended scope of the invention as defined by the following claims.

What I claim as new and desire to secure by letters Patent of the United States is:

1. A method for producing crystal boules having extensive flat, parallel facets which are microscopically smooth comprising the steps of

selecting a seed crystal of the material to be grown and having a pair of parallel surfaces which are strongly faceting,

forming a melt of the material comprising the seed crystal,

contacting the seed crystal with the surface of the melt for a period of time sufficient to wet the seed crystal and thereby establish a crystal-melt interface,

orienting the seed crystal in a particular crystallographic direction such that the strongly faceting and nonfaceting surfaces thereof are respectively normal to axes of rapid and slow temperature changes respectively with distance from the seed crystal center along the crystal-melt interface,

establishing a particular symmetric anisotropic temperature distribution at the crystal-melt interface relative to the seed crystal orientation by means of an external heat source distributing heat to the growing crystal boule from planar faces open at their ends and arranged parallel to the axis of slow temperature change consistent with the faceting surfaces wherein the symmetric anisotropic temperature distribution consists of

increasing the temperature along the crystal-melt interface slowly with increasing distance from the center of the crystal boule being grown from the seed crystal along a first axis defining the crystal boule width, and

increasing the temperature along the crystal-melt interface with increasing distance from the center of the crystal boule along a second axis perpendicular

to the first axis and which defines the crystal boule thickness,

withdrawing the seed crystal from the melt at a predetermined rate in a direction normal to the crystal-melt interface while maintaining the anisotropic temperature distribution at the crystal-melt interface during the growth process of the crystal boule, and

preventing the crystal boule from rotating with respect to the symmetry axes of the anisotropic temperature distribution while withdrawing the crystal boule to thereby cause the growth of a crystal boule having a pair of extensive flat, accurately parallel facet surfaces which are microscopically smooth.

2. The method set forth in claim 1 wherein

the step of increasing the temperature with increasing distance from the center of the crystal boule along the second axis consists of

increasing the temperature at substantially the same slow rate as the temperature along the first axis for a distance up to $t/2$ where t is the crystal boule thickness, and increasing at a substantially faster rate for distances beyond $t/2$ from the center of the crystal boule, the particular symmetric anisotropic temperature distribution and crystal boule orientation causing the crystal boule to preferably vary in dimension along the first axis rather than along the second axis in response to inherent small temperature fluctuations at the crystal-melt interface.

3. The method set forth in claim 1 and further comprising the step of

cutting the grown crystal boule to predetermined dimensions to thereby utilize the crystal formed by the cutting process in a device requiring two surfaces that are flat, microscopically smooth, free from mechanical damage and accurately parallel, the microscopically smooth surfaces requiring no further polishing or cleaving process whereby the crystal is utilized directly in the device.

4. The method set forth in claim 1 wherein

the step of establishing a particular symmetric anisotropic temperature distribution consists of establishing first temperature zones slightly higher than the average melt temperature along the crystal-melt interface associated with nonfaceting surfaces of the crystal boule whereby the temperature increases slowly with increasing distance from the center of the crystal boule along the first axis thereof, and

establishing equal second temperature zones higher than the first temperature along the crystal-melt interface associated with the pair of strongly faceting surfaces of the crystal boule whereby the temperature increases rapidly with increasing distance from the center of the crystal boule along the second axis thereof.

5. The method set forth in claim 4 wherein

the step of orienting the seed crystal consists of aligning the first axis of the seed crystal with the normal to the nonfaceting surfaces of the seed crystal, and aligning the second axis of the seed crystal with the normal to the faceting surfaces of the seed crystal,

the symmetric anisotropic temperature distribution and crystal orientation causing the growing crystal boule to vary in dimension preferably along the

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nonfaceting surfaces thereof and thereby substantially avoid formation of growth steps on the faceting surfaces in response to inherent small temperature fluctuation at the crystal-melt interface whereby the faceting surfaces are microscopically smooth along extensive regions thereof.

6. The method set forth in claim 4 wherein the step of establishing the particular symmetric anisotropic temperature distribution consists of

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disposing an auxiliary heating device spaced slightly above the top surface of the melt and arranged with the heating element thereof parallel to, and spaced slightly from, the facet surfaces of the seed crystal and resultant crystal boule which is withdrawn from the melt between portions of the auxiliary device heating element.

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