Feb. 27, 1968 J. W. FAUST, JR 3,370,927

METHOD OF ANGULARLY PULLING CONTINUOUS DENDRITIC CRYSTALS

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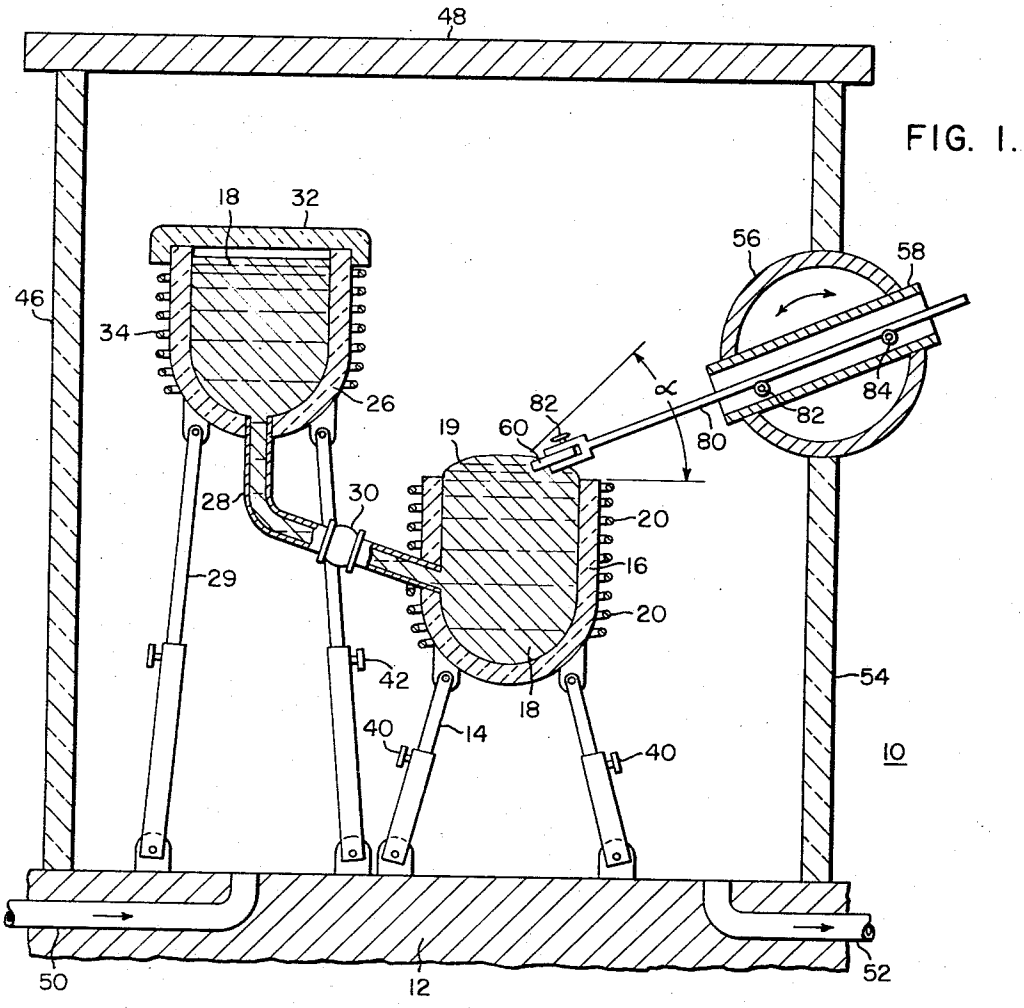


FIG. 1.

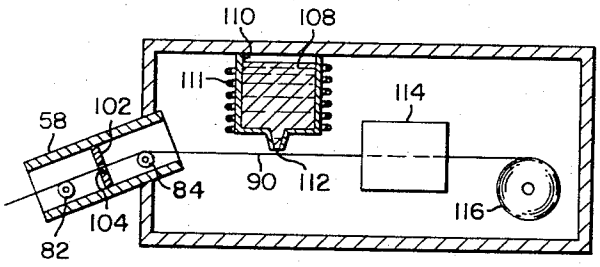


FIG. 3.

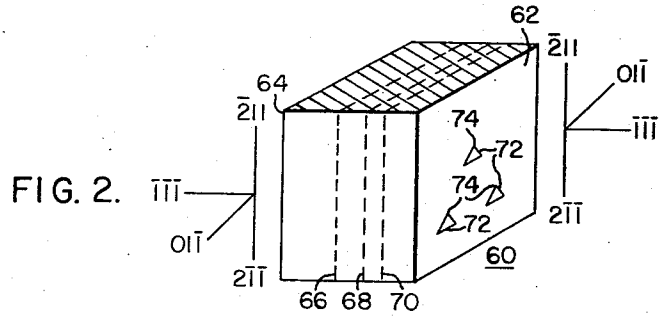


FIG. 2.

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METHOD OF ANGULARLY PULLING CONTINUOUS DENDRITIC CRYSTALS

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This invention relates to a process for growing dendritic crystals of solid materials of indenfinite length and particularly refers to dentritic crystals of semiconductor materials.

In the past, as set forth in U.S. Patent 3,031,403, dendrite crystals have been grown from a supercooled melt by contacting the melt with the particular type of seed which had its <211> direction vertical or perpendicular to the melt surface. The resultant dendrite was grown or pulled from the melt in a vertical direction.

This process readily lends itself to growing dendritic crysals of almost indefinite length. This resulted in the problem of what to do with the grown dendrite. Since the dendrite was found to be relatively flexible, the problem was solved by rolling the dendrite on a storage roller in a top compartment of the furnace. While this solution was satisfactory, it did require a furnace of considerable height and a storage chamber increased the size, weight and cost of the furnace. More important, it also required the dendrite to be bent in a 90° angle to the pull direction as it was received by the roller and this was not always satisfactory.

Further, if one wanted to form p-n junctions in a length of dendritic crystal as it was grown. either by alloying or vapor diffusion, the furnace had to be equipped with still another chamber which further increased the height of the furnace. These problems were all the result of the necessity of contacting the melt surface in a perpendicular direction to the melt surface and withdrawing the seed in a perpendicular direction relative to the melt surface.

An object of the present invention is to provide an improved process for growing dendritic crystals of substantially indefinite length.

Anther object of the present invention is to provide a process in which the seed crysal contacts the melt surface at an angle considerably less than 90°.

Other objects of the invention will, in part, be obvious and will, in part, appear hereinafter.

FIG. 1 is a view in elevation, partly in cross section, of a crystal growing apparatus in accordance with this invention;

FIG. 2 is a greatly enlarged fragmentary view of a dendritic crystal having three twin planes and suitable for use as a seed in accordance with the teachings of this invention; and

FIG. 3 is a view, in elevation and partly in section, of a processing chamber suitable for use in accordance with the furnace chamber of FIGURE 1.

In accordance with the present invention, it has been found that crysatls of solid materials may be prepared as flat dendritic crystals having a closely controlled thickness with relatively precise flat parallel faces. These flat dendritic crystals may be pulled or grown from melts of the material at a relatively high rate of speed or pulling of the order of one hundred times and greater than the linear pulling velocity previously employed in the art. The thickness of the crystals may be readily controlled and surface imperfections minimized or reduced by following the teachings of the present invention.

In practicing the process, a melt of the material to be grown into a flat dendritic crystal is prepared at a temperature slightly above the melting temperature thereof.

The surface of the melt is contacted with a previously prepared crystal having at least one twin plane and preferably three at the interior thereof, the crystal being oriented with the <211> direction contacting the melt surface at an angle of from 45° to substantially zero degrees.

Other necessary or desirable crystallographic and physical features of the seed crystals will be pointed out in detail hereinafter. The seed crystal is dipped into the surface of the melt a sufficient period of time to cause wetting of the lower surface of the seed, usually a period of time a few seconds to a minute is adequate. and, then, the melt is supercooled rapidly following which the seed crystal is withdrawn with respect to the melt at the speed of the order of from 1 to 10 inches per minute. Under some conditions considerably slower pulling speeds than an inch per minute can be employed, for example 0.2 inch per minute. Pulling speeds of from 10 to 25 inches per minute have given good results. The degree of supercooling and the rate of pulling can be readily so correlated that the seed crystal withdrawn from the melt comprises solidified melt material thereon of a precisely desired thickness and the desired crystallographic orientation.

The present invention is particularly applicable to solid materials crystallizing in a diamond cubic lattice structure. Examples of such materials are the elements silicon and germanium. Likewise, stoichiometric compounds having an average of 4 valence electrons per atom respond satisfactorily to the growing process. Such compounds which have been processed with excellent results comprise substantially equal molar proportions of an element from Group III of the periodic table, and particularly aluminum, gallium and indium, combined with an element from Group V of the periodic table, and particularly phosphorus, arsensic and antimony. Compounds comprising stoichiometric proportions of Group II and Group VI elements for example ZnSe and ZnS, can be processed. These materials crystallizing in the diamond cubic lattice structure are particularly satisfactory for various semiconductor applications. Furthermore, the diamond cubic lattice structure materials may be intrinsic or may be doped with from one or more impurities to produce n-type or p-type semiconductor material. The crystal growing process of the present invention may be applied to all these different materials.

For a better understanding of the practice of this invention reference should be had to FIGURE 1 of the drawings wherein there is illustrated apparatus **10** for practicing the process.

The apparatus **10** comprises a base **12** carrying a support **14** for crucible **16** of a suitable refractory material such as graphite to hold a melt **18** comprised of a semiconductor material from which the dendrite crystal is to be drawn. Melt **18**, for example, germanium is maintained within the crucible **16** in the molten state by suitable heating means such, for example, as an induction heating coil **20** disposed about the crucible. Controls, not shown are employed to supply alternating electrical current to the induction coil **20** to maintain a closely controlled temperature in the body of the melt **18**. The temperature should be readily controllable to provide a temperature, within the melt, a few degrees above the melting point thereof, and also to enable the temperature to drop in a few seconds, for example in five to fifteen seconds, to a temperature at least one degree below the melting temperature, and preferably to supercool the melt from 5° C. to 50° C., or even lower.

A second crucible **26** of a suitable refractory material such as graphite is supported on a base **12** by a support member **29**. The crucible **26** contains an additional quantity of melt **18** which may be charged into the crucible

16 to a suitable conduit 28 by an actuating valve 30 operated by electromagnetic controls (not shown) or by any other suitable means. A conduit 28 is preferably connected to crucible 16 in such a manner so as to supply molten material to the bottom portion of the charge 18 therein so that it can obtain the desired temperature before reaching the surface 19. The crucible 26 has a cover 32 and is surrounded by heating means, such for example as an induction heating coil 34. Controls, not shown, are employed to supply alternating electrical current to the induction coil 34 to maintain a closely controllable temperature in the melt 18 within the crucible 26. The temperature of the melt within the crucible 26 should be a few degrees above the melting point of the material. The melt within crucible 26 is used to replenish the melt in crucible 16. While crucible 26 has been illustrated in FIGURE 1 in a particular relation to crucible 16, it will be understood that crucible 26 may be disposed anywhere within the apparatus 10. It will also be understood that depending upon the length of dendrite to be grown and processed, and the capacity of crucible 16, it may be necessary to employ an auxiliary crucible such as the crucible 26. Sufficient material is present in crucible 16 to enable the desired amount of dendrite to be pulled therefrom.

Supports 14 and 29 for crucibles 16 and 26 respectively have means 40 and 42 respectively for adjusting their respective height.

A protective enclosure 46 of graphite, quartz, metal or other suitable material is disposed completely about the crucibles 16 and 26 and a cover 48 closes the top thereof.

Within the base 12 there is a conduit 50, and if necessary, a vent 52 for introducing or circulating a current of a protective gas atmosphere into the enclosure 46 if desired. Depending on the crystal material being processed in the apparatus, the protective atmosphere may comprise a noble gas, such as helium or argon, a reducing gas such as hydrogen or mixtures of hydrogen or nitrogen or the like, or mixtures of two or more gases. In most cases, the interior of apparatus 10 will be evacuated to a high vacuum of at least 10 microns absolute, and preferably below 1 micron, in order to produce original and processed crystals free from any gas.

In the event that the process applied to compounds having one component with a high vapor pressure at the temperature of the melt, a separately heated vessel containing the component may be disposed in the enclosure 46 to maintain therein a vapor of such component at a partial pressure sufficient to prevent impoverishing the melt of the grown crystal with respect to that component. Thus, an atmosphere of arsenic may be provided when doped to intrinsic crystals of gallium arsenide or being pulled. The enclosure 46 may be suitably heated, for example, by an electrically heated blanket or wrapping to maintain the walls thereof at a temperature above the temperature of the separately heated vessel containing the arsenic in order to prevent condensation of the arsenic thereon.

Wall 54 of enclosure 46 has a rotatable portion 56 through which passes a tube 58. The significance of rotational portion 56 and the tube 58 will be described in detail hereinafter.

With reference to FIGURE 2, there is illustrated a seed crystal 60 suitable for use in accordance with the teachings of this invention. The seed crystal 60 comprises two relatively flat parallel faces 62 and 64 and three interior twin planes 66, 68 and 70 extending across the entire cross section thereof.

Examination will show that the crystallographic structure of the preferred seed on both faces 62 and 64 is that indicated by the crystallographically direction arrows at the right and left faces respectively of the figure.

If the faces 62 and 64 of the dendrite crystal 60 were to be etched preferentially to the {111} planes, they will both exhibit equilateral triangle shaped etch pits 72 whose vertices 74 will point upwardly and whose bases will be parallel to the surface of the melt.

A non-twin crystal or a crystal containing two twin planes or any even numbers thereof will exhibit triangular each pits on faces whose vertices will be pointing opposite to the direction of the vertices on the other face.

Most satisfactory crystal growth is obtained by employing seed crystals of the type exhibited in FIG. 2. Such a crystal contains three twin planes.

Seed crystals having an odd number (other than one and three, that is, five, seven and up to thirteen or more) twin planes containing the growth direction may be employed in practicing the process of this invention, due care being had to point the triangular etch pits on the outer faces of the crystal with their vertices upwardly and the bases parallel to the surface of the melt. Further, seed crystals containing an even number of twin planes may be employed for crystal pulling, though as desirable pulled crystals will not be obtainable as with the preferred three twin plane seed crystals shown in FIGURE 2. Normally, the pulled dendrite will exhibit the same twin plane structure as the seed crystal exhibits. Thus, the dendrite will have three twin planes extending through its entire length if the seed comprises three twin planes.

In the operation of the apparatus 10 of FIGURE 1 the seed crystal 60 of FIGURE 2 is connected to a pull rod 80 by means of a screw 82 or the like. The seed 60 and pull rod 80 are passed through the tube 58 and rotational portion 56 of wall 54. Rather than pull rod 80 the seed crystal may be butt soldered or otherwise joined to one end of a leader tape. Such a leader tape may be of steel or any other suitable material or may be comprised of a previously grown dendride. In this last case, the previously grown dendrite will function as a seed. It is preferable, but not necessary, that the tape have the same width and thickness as that of the dendrite to be grown.

The pull rod or leader tape employed with the seed 60 attached passes over guide rollers 82 and 84 in the tube 58 until the seed 60 contacts the surface 19 of the melt 18.

The angle, shown as alpha in FIGURE 1, at which the {211} plane of the seed 60 meets the melt may vary from as near to zero as is physically possible because of apparatus limitations to 45°. The top surface 19 of the melt 18 should extend above the top of the crucible 16. The surface tension of semiconductor materials is such that this is possible.

The melt 18, which is slightly above its melting point, dissolves the tip of the seed crystal, a meniscus-like contact between the molten top of the seed crystal and the melt is formed.

The power input to the heating coil 20 is now reduced in order to supercool the melt (or by reducing the applied heat if other modes of heat applications and induction heating are employed). There will be observed in the period of time the order of five seconds after the heat is reduced to a cruclible of about 2 inches in diameter and two inches in length, the supercooling being about 8° C. an initial elongated hexagonal growth or enlargement on the surface of the melt adjoining the tip of the seed crystal. The hexagonal surface growth increases in area so that in approximately ten seconds after heat input is reduced its area is approximately three times that of the cross section of the seed crystal. At this stage, there will be evident spikes growing out of the two opposite hexagonal vertices lying in the plane of the seed. These spikes appear to grow at a rate of approximately 2 millimeters per second. When the spikes are from 2 to 3 millimeters in length, the seed pulling mechanism (not shown) is energized to pull the crystal from the melt at a desired rate for example, five inches per minute. The initiation of pulling is timed to the appearance and growth of the spikes for best results.

After pulling the seed crystal from the supercooled melt, it will be observed that the first solid diamond shaped area portion is attached to the seed crystal and that a downwardly extending dendrite crystal has formed at each end of the elongated diamond area adjacent the spike. Accordingly, two dendrite crystals can be readily pulled from the melt at one time from the single seed crystal. For the purpose of this invention, it is preferred to pull only a single dendrite **90** from the melt. The control of the width and thickness posed problems that can thus be handled with single dendrites. Therefore, by manipulation of the conditions under which the crystal is grown, one of the crystals is stunted and ceases to grow.

The dendrite so grown passes through the tube **58** and rotational portion **56** of wall **54** and out of the furnace. The dendrite so grown may be cut into any desired length as it passes from the furnace.

The angle alpha at which the seed **60** meets the surface **19** of the melt **18** is controlled or adjusted by the rotational portion **56** of wall **54** of the chamber. Adjustable means **40** and **42** are employed to make any desired changes in the height of the crucibles **16** and **26** respectively.

With reference to FIGURE 3, if it is desired, the dendrite **90** can be passed directly from the furnace **10** into a chamber **100**. The chamber **100** is sealed off from the furnace **10** by shield **102** which has a passageway **104** therein through which the dendrite **90** passes.

The chamber **100** can contain an atmosphere of a gas suitable for doping the dendrite to produce either a p-type on n-type semiconductivity within the dendrite. Suitable dopants are well known to those skilled in the art. If desired a vessel **110**, for example, a crucible, can be disposed in the chamber **100** in close proximity to the dendrite **90**. The vessel **110** contains a molten material **108** which is deposited upon at least one contaminant-free surface of the dendrite **90**. The material **108** is held at a temperature above its melting point by heating coil **111** or other suitable heating means disposed about the vessel **110**. As the dendrite **90** passes the vessel **110**, the material **108**, in a vaporized form, passes from the vessel **110** through an opening **112** therein and impinges upon and is deposited upon at least one surface of the dendrite **90**. Examples of materials which may be vapor deposited upon at least one surface of a dendrite crystal in accordance with the process of this invention includes the p-type and n-type dopants known to those skilled in the art of semiconductors, for example, p-type dopants, boron, aluminum, gallium, indium; n-types dopants phosphorus, arsenic, antimony and bismuth. In addition, the melt **108** may include neutral metals or elements such as tin, gold and silver. Vapors of the dopant in a neutral metal will deposit as an alloy on the dendrite surface. It will be understood that two or more dopants may be deposited in the form of an alloy at the same time. For example, a boron-gold-bismuth alloy may be deposited on the surface of the dendrite in accordance with the teachings of this invention.

After the deposition of the material **108** upon the dendrite **90**, the dendrite passes through a fusion furnace **114**. Within the fusion furnace **114** the deposited coating material melts and alloys with a portion of the dendrite. It will be understood that only a fraction of the thickness of the dendrite is dissolved by the molten deposited material. Diffusion of the coating material into the dendrite also occurs. As the dendritic strip leaves the furnace, it cools, whereby the molten material or dendritic material resolidifies with the portion of the positive material distributed within the recrystallized material, whereby, a semiconductor transition zone of p-n junction is formed within the dendrite.

The dendrite **90** is then wound onto the roller **116**. To prevent the dendrite from being scratched as it is taken up by the roller **116** a plastic inner layer, for example, a thin film, foil or tape of for example polyethylene, polytetrafluoroethylene, polytrifluoromonochloroethylene, nylon or the like may be disposed about or between each succeeding layer of dendrite. The plastic strip may be formed of a flat depression in the middle of either or both sides to act as a spacer. The plastic strip will also serve to keep the dendrite in place if there should be a break during the drawing and processing step. In a modification of the process described immediately hereinabove, the dendrite may be removed directly from the furnace and processed in accordance with any of the steps known to those skilled in the art of semiconductors.

In following the teachings of this invention, the height of the furnace chamber is substantially reduced from that previously required and in addition a dendritic crystal of almost indefinite length may be drawn and rolled for storage without ever being stressed as a result of going through a substantially 90° angle as it enters onto a roller.

The following examples are illustrative of the present invention:

Example I

In apparatus similar to FIGURE 1, a graphite crucible containing a quantity of intrinsic germanium is heated by the induction coil to a temperature several degrees above the melting point of germanium, the temperature being of about 938° C., until the entire quantity forms a molten pool. A dendritic seed crystal having three interior twin planes extending entirely therethrough and oriented as in FIGURE 2 of the drawing, held in a holder is lowered until its lower end touches the surface of the molten germanium at an angle of 40° from the horizontal. The contact with the molten germanium is maintained until a small portion of the end of the dendritic seed crystal has melted. Thereafter the temperature of the melt is lowered rapidly in a manner of five seconds by reducing current to the coil to a temperature of 8° below the melting point of the germanium so that the melt is supercooled (about 928° C.). After an interval of approximately ten seconds of this temperature, the germanium seed crystal is pulled at a rate of seven inches per minute. The dendritic crystal is attached to the seed at a thickness of seven mills of approximately two millimeters in width. The grown dendritic crystal has substantially flat highly parallel faces from end to end with {111} orientation. The germanium dendritic crystal so grown was found to have no surface imperfections except for a number of microscopic steps differing by about 50 angstroms and was of a quality suitable for semiconductor applications. Particularly good results were had with the seed crystal at three interior twin planes separated by a distance of 5 microns and 1⅔ microns respectively. The dendrite, of course, similarly had three twin planes.

The process of Example I was repeated, except for increasing the pull rate to 12 inches per minute. The dendritic crystal was approximately 3.5 mils in thickness and a width of about 30 mils. The surface imperfections and flatness were exceptional. Thus in a length of an inch there was observed less than a wavelength of light variation and thickness. The faces of the dendritic crystal were precisely {111} orientation.

Example II

The process of Example I was repeated with the seed forming an angle of 20° from the horizontal and a pull rate of approximately 4 inch per minute. The dendrite so grown had a thickness of 10 mils and was approximately 35 mils in width.

Example III

The process of Example I was again repeated with the seed forming an angle of 10° from the horizontal and at a pull rate of 4. The dendrite thus grown had a thickness of 8 mils and a width of 40 mils. The faces of the dendrite crystal thus produced were precisely {111} orientation and were highly suitable for the use of fabrication of semiconductor devices.

It will be understood, the above description and drawings are only illustrative and not limiting. It will be further understood that while the above description emphasized the application of the present invention to semiconductor materials the process may be employed for producing grown dendritic crystals from any metal or alloy or compound of zinc blend structure and growable from a melt. By the practice of the present invention, flat crystals of high perfection of orientation may be produced by the practice of the process disclosed herein.

I claim as my invention:

1. In the process of producing thin crystals of a solid material crystallizing in a diamond cubic lattice structure selected from the group consisting of silicon, germanium, and stoichiometric compounds having an average of 4 valence electrons per atom, the steps comprising melting a quantity of the material, bringing the melt to a temperature slightly above the melting point of the material, contacting a surface of a melted material with a seed crystal of the material for a period of time to wet the seed crystal with the melt material, the seed crystal having a plural odd number of parallel interior twin planes, the seed crystal contacting the melt surface at an angle of from substantially 0 to 45° of the horizontal, the twin planes being parallel to the <211> direction, the dendritic crystal when etched exhibiting triangular etch pits on both faces with the vertices of the triangular pits being directed upwardly with respect to the melt and the faces of the etch pits being parallel to the melt surface, supercooling the melted material to a selected temperature, and pulling the seed crystal at the rate of the order of at least 1 inch per minute with respect to the melt surface while maintaining the selected temperature whereby the material from the melt solidifies on the seed crystal and produces an elongated flat dendritic crystal.

2. The process of claim 1 in which the seed crystal is withdrawn from the melt at a rate of from 1 to 10 inches per minute.

3. In the process of producing thin flat crystals of a solid material crystallizing the diamond cubic lattice structure selected from a group consisting of silicon, germanium, and stoichiometric compounds having an average of four valence electrons per atom, the steps comprising melting a quantity of the material confined within a crucible, the surface of the melt extending above the top of the crucible, bringing the melt to a temperature slightly above the melting point of the material, contacting a surface of a melting material with a seed crystal of the material for a period of time to wet the seed crystal with the melted material, the seed crystal having a plural odd number of parallel interior twin planes, the seed crystal contacting the melt surface in an angle off the horizontal sufficient to clear the side of the crucible but not exceeding 45°, the twin planes being parallel to the <211> direction, the dendritic crystal when etched exhibiting triangular etch pits on both faces with the vertices of triangular etch pits being directed upward with respect to the melt and the faces of the etch pits being parallel to the melt surface, supercooling the melted material to a selected temperature, and pulling the seed crystal from the melt at a rate of the order of at least one inch per minute of the melt surface while maintaining the melt at the selected temperature, the rate of withdrawal being correlated to the degree of supercooling so that the material from the melt solidifies on the seed crystal in the form of a flat dendritic crystal.

4. The process of claim 3 in which the seed crystal contacts the melt surface at an angle of from substantially 0 to 45° off the horizontal.

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