April 14, 1964 S. N. DERMATIS ETAL 3,129,061

PROCESS FOR PRODUCING AN ELONGATED UNITARY BODY OF
SEMICONDUCTOR MATERIAL CRYSTALLIZING IN THE
DIAMOND CUBIC LATTICE STRUCTURE
AND THE PRODUCT SO PRODUCED

Filed March 27, 1961 2 Sheets-Sheet 1

Fig. 1.

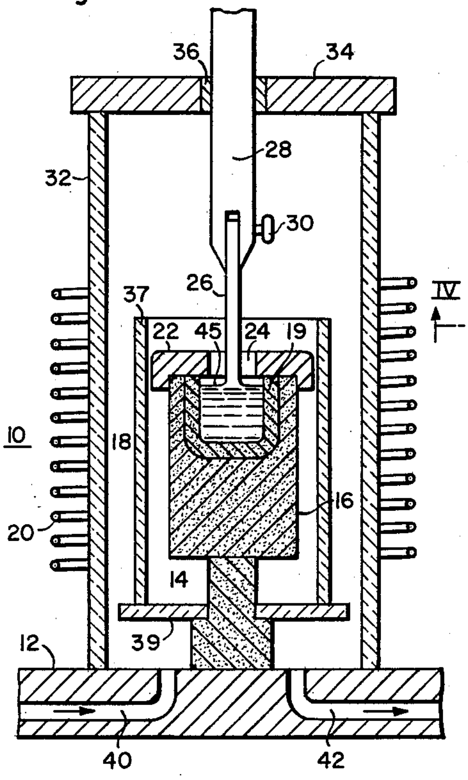
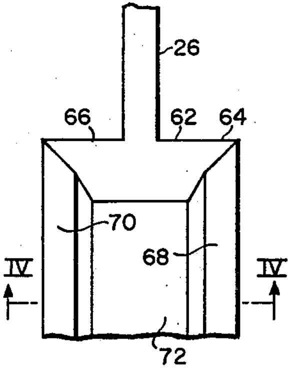


Fig. 3.



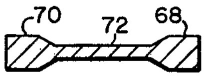


Fig. 4.

Fig. 7.

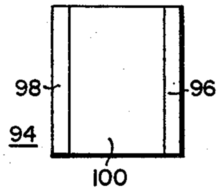


Fig. 8.

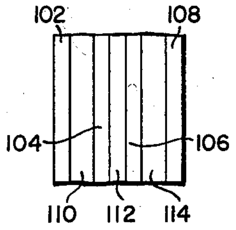


Fig. 2.

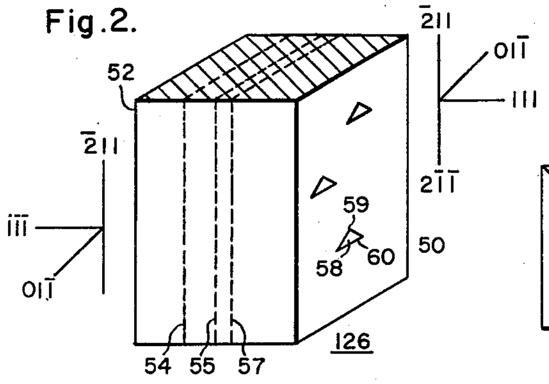


Fig. 5.

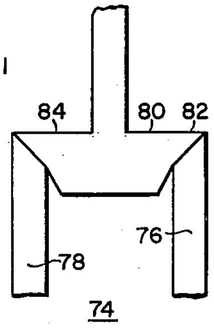
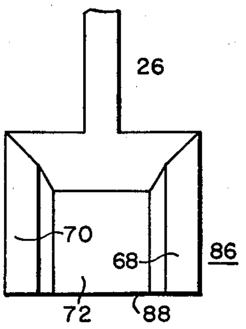


Fig. 6.



WITNESSES

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2 Sheets-Sheet 2

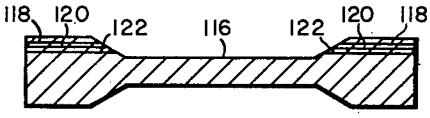

Fig. 9.

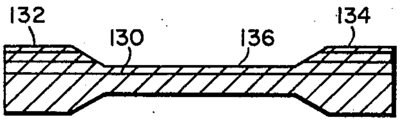

Fig. 10.

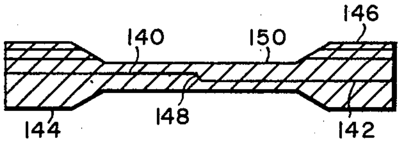

Fig. 11.

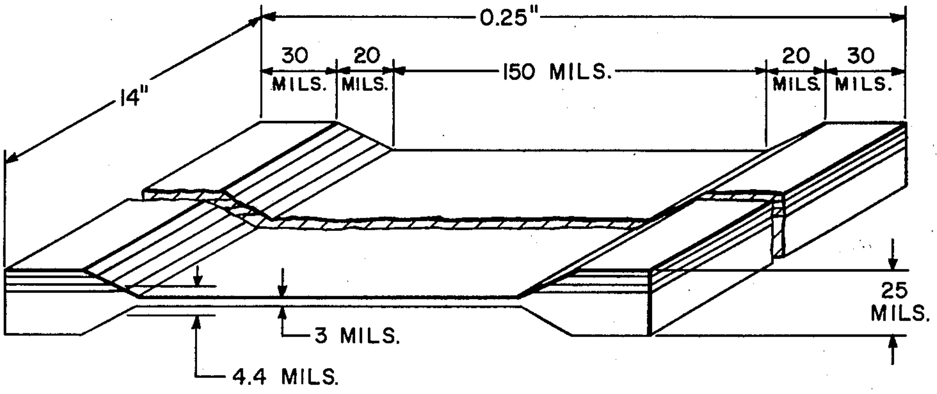

Fig. 12.

3,129,061

PROCESS FOR PRODUCING AN ELONGATED UNITARY BODY OF SEMICONDUCTOR MATERIAL CRYSTALLIZING IN THE DIAMOND CUBIC LATTICE STRUCTURE AND THE PRODUCT SO PRODUCED

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17 Claims. (Cl. 23—223.5)

This invention relates generally to a grown or pulled crystalline sheet of a material crystallizing in the diamond cubic lattice structure and semiconductor materials in particular, and to a process for growing or pulling the same.

Elongated dendritic crystals of materials crystallizing in the diamond cubic lattice structure have been grown, and the crystals and process for growing them has been set forth in detail in U.S. patent application, Serial No. 844,288, filed October 5, 1959, and assigned to the same assignee as the present application, now U.S. Patent 3,031,403.

In growing two or more dendrites of a semiconductor material simultaneously from a single seed in accordance with the process set forth in U.S. patent application, Serial No. 844,288, it has been found that the two dendrites sometimes grow together or the space between the several dendrites is sometimes uncontrollably partially bridged by spikes or other lateral crystal growth of solidified material from the melt. The solidified material accidentally formed between the dendrites proper has been almost invariably irregular, thick, has a rough surface, and contains a large number of dislocations. Because of these gross defects none of these grown configurations provides a body of a semiconductor material which is suitable for any use such as the fabrication of semiconductor devices. Consequently, the growth of dendrites from a seed has been so controlled as to provide for only a single dendrite being pulled at one time.

The surprising discovery has now been made that under controlled conditions an outstandingly useful body of a semiconductor material can be prepared which is comprised of two or more dendritic crystals joined crystallographically by an almost perfect continuous, wide and thin web or sheet which is substantially dislocation free. The surfaces of this web have the (111) crystal orientation.

An object of the present invention is to provide an elongated body of a material crystallizing in the diamond cubic lattice structure comprised of at least two parallel elongated dendritic crystals joined crystallographically into a unitary body by a thin web portion extending between the dendritic crystals along the length of the body.

Another object of the present invention is to provide an elongated body of a material crystallizing in the diamond cubic lattice structure comprised of at least two parallel elongated dendritic crystals joined crystallographically into a unitary body by a thin web portion extending between the adjacent dendritic crystals over the length of the body, with a plurality of twin planes extending at least through the dendritic crystals.

Another object of the present invention is to provide an elongated body of a material crystallizing in the diamond cubic lattice structure comprised of at least two parallel elongated dendritic crystals joined crystallographically into a unitary body by a thin web portion extending between the dendritic crystals over the length of the body, there being a plurality of twin planes extending through the dendritic crystals portion over the entire length of the dendrites and across the width of the entire body.

A still further object of the present invention is to provide an elongated unitary body of a semiconductor material comprising a central portion and two edge portions, said central portion being comprised of a thin, flat sheet of substantially dislocation free, single crystal, semiconductor material crystallographically joined to the edge portions, each of said edge portions being comprised of a dendritic crystal of the semiconductor material, said central portion having a highly uniform thickness over the length of the body, and said edge portion being substantially uniformly spaced over the length of the body.

Another object of the invention is to provide a process for producing an elongated body of material crystallizing in the diamond cubic lattice structure comprising pulling at least two closely spaced parallel elongated dendrites from a supercooled melt of the material at a relatively low pulling rate whereby a relatively thin flat sheet or web of solidified material joins the dendrites.

A still further object of the present invention is to provide a process for producing an elongated body of a material crystallizing in the diamond cubic lattice structure comprised of at least two parallel elongated dendritic crystals, said dendritic crystals being joined crystallographically into a unitary body by a thin web portion of the same semiconductor material extending between the dendritic crystals, comprising the steps of melting a quantity of the material, bringing the melt to a temperature slightly above the melting point of the material, contacting a surface of the melted material with at least a surface of a seed crystal of the material for a period of time sufficient to wet the seed crystal wih the melted material, the seed crystal having at least two twin planes extending across at least a portion of the surface in contact with the melt, the seed crystal being oriented with a <111> direction parallel to the surface of the melt and a <211> direction perpendicular to the surface of the melt, the twin planes being parallel to the <211> direction, super cooling at least a portion of the melt to a temperature 5° C. to 10° C. below the melting point, the surface area of the supercooled portion being at least 0.25 sq. in. on the surface of the melt, and pulling the seed crystal from the melt at a rate of from approximately ¼ inch per minute to 4 inches per minute, whereby the material from the supercooled portion of the melt solidifies on the seed crystal and produces an elongated body comprised of at least two dendritic crystals crystallographically joined throughout the length of the body by a thin web of material.

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

For a better understanding of the nature and objects of the invention, reference should be had to the following detailed description and drawings, in which:

FIGURE 1 is a view in elevation, partly in section, of a crystal growing apparatus suitable for use in accordance with the teachings of this invention;

FIG. 2 is a greatly enlarged fragmentary view in elevation of a seed suitable for use in accordance with the teachings of this invention;

FIG. 3 is an enlarged fragmentary view in elevation of a body of material being grown in accordance with the teachings of this invention;

FIG. 4 is a cross-sectional view of the body of FIG. 3 taken along the line IV—IV thereof;

FIGS. 5 and 6 are greatly enlarged fragmentary views in elevation of alternative seeds suitable for use in accordance with the teachings of this invention;

FIG. 7 is a fragmentary view in elevation of a body prepared in accordance with the teaching of this invention;

FIG. 8 is a fragmentary view in elevation of a modified body prepared in accordance with the teachings of this invention;

FIGS. 9, 10 and 11 are cross-sectional views of bodies of material prepared in accordance with the teachings of this invention; and

FIG. 12 is a view in perspective of a body of material prepared in accordance with the teachings of this invention.

In accordance with the present invention and attainment of the foregoing objects there is provided an elongated sheet-like body of a semiconductor material crystallizing in the diamond cubic lattice structure comprised of at least two parallel elongated dendritic crystals spaced apart up to one-half inch and more joined crystallographically into a unitary body by a thin web portion of the same semiconductor material extending between the dendritic crystals over the entire length of the body.

The elongated body of semiconductor material of this invention can be prepared by melting a quantity of the material to be grown, contacting a surface of the melted 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 at least two parallel twin planes which come into contact with the melt, the seed crystal being oriented with a <111> direction parallel to the surface of the melt and a <211> direction perpendicular to the surface of the melt, the twin planes being parallel to the <211> direction and the <111> plane of the seed, the melt being supercooled to a temperature of at least about 5° C. below the melting point, the surface area of the supercooled portion being at least about 0.25 sq. in., initiating growth of at least parallel dendrites from the seed, and pulling the seed crystal with at least two parallel dendrites attached thereto from the melt at a rate of from approximately ¼ inch per minute to 4 inches per minute whereby a thin flat web joins the parallel dendrites crystallographically.

More particularly, in a preferred practice of the process of this invention, a melt of the material to be grown into an elongated body comprised of at least two parallel elongated dendritic crystals crystallographically joined into a unitary body by a thin web or sheet portion extending between the dendritic crystals over the entire length of the body is prepared at a temperature slightly above the melting point thereof. The surface of the melt is contacted with a previously prepared seed whose configuration and orientation will be discussed in detail hereinafter. The seed comprises at least two parallel twin planes disposed perpendicularly to the surface of the melt. The seed 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 of a few seconds to a minute is adequate, the twin planes also being in contact with the melt, and, then, at least that portion of the melt immediately adjacent to the seed is supercooled rapidly to provide a surface of an area of at least about 0.25 sq. in. of supercooled liquid melt, at least two parallel dendrites should be formed on the seed, following which the seed crystal is withdrawn from the supercooled portion of the melt at a speed of about from ¼ inch to 4 inches and, preferably, at a speed of from ¼ inch to 1 inch per minute. The degree of supercooling which is preferably from 5° C. to 10° C. for silicon and the rate of pulling can be readily correlated so that the seed withdrawn from the melt comprises an elongated body consisting of the parallel elongated dendritic crystals and crystallographically joining them into a unitary body, a thin web or sheet portion which extends between the dendritic crystals over the entire length of the body.

The present invention is particularly applicable to solid materials crystallizing in the diamond cubic lattice structure. Examples of such materials are the elements silicon and germanium. Likewise, stoichiometric compounds having an average of four valance electrons per atom respond satisfactorily to the crystal growing process of this invention. 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, arsenic 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 they may be doped with one or more impurities to produce n-type or p-type semiconductor materials, or bodies having a p-n-p or n-p-n cross-section. The crystal growing process of the present invention may be applied to all of these different materials.

For a better understanding of the practice of this invention, reference should be had to FIG. 1 of the drawing wherein there is illustrated apparatus **10** for practicing the teachings of this invention. The apparatus **10** comprises a base **12** carrying a graphite support **14** for a susceptor or crucible **16** of a suitable refractory material such as graphite to hold a melt of the material which will be referred to hereinafter as silicon from which is to be grown or pulled the elongated body comprised of at least two parallel elongated dendritic crystals crystallographically joined into a unitary body by a thin web or sheet portion extending between the dendritic crystals over the entire length of the body. Molten silicon **18** is maintained within a quartz lining **19** within the susceptor **16** in the molten state by a suitable heating means such, for example, as a radio frequency (RF) induction heating coil **20** disposed about the susceptor **16**. Other heating means may be employed such as radiation, electron beam or a combination thereof. The best temperature control and results are realized when the RF coil extends above the top of the susceptor **16**. A suitable source of energy and control means, not shown, are employed to supply an alternating electrical current, for example, from 100 kc. to 5 megacycles, to the RF coil **20** to maintain a closely controlled temperature in the body of the melt **18**. The energy input should be readily controllable so as to provide at the proper time a temperature in the melt a few degrees above the melting point and also to reduce the heat input so that the temperature drops in a few seconds, for example, in 5 to 10 seconds to a temperature at least 1 degree below the melting temperature and preferably to supercool at least a portion of the melt from 5 to 10° C. An apertured cover **22**, comprised of a suitable material such as for example, molybdenum, tantalum or tungsten, closely fitting the top of the susceptor **16**, is provided in order to maintain a low thermal gradient above the top of the melt. Passing through an aperture **24** in the cover **22** is a seed and attached growth **26**. The seed **26** is fastened to a pulling rod **28** by means of a screw **30** or the like. The pulling rod **28** is actuated by a suitable mechanism (not shown, but are well known in the crystal growing art) to control its upward movement at a desired uniform rate, ordinarily at a rate of from ¼ inch to 4 inches per minute. A protective enclosure **32** of glass or other suitable material is disposed about the susceptor **16** and between the susceptor **16** and the RF coil **20** with a cover **34** closing the top thereof except for a sealing aperture **36** through which the pulling rod **28** passes. A heat shield **37**, comprised of, for example quartz, is disposed within enclosure **34** and is mounted on a base **39**, which in turn is suspended from the support **14**, surrounds the susceptor **16**.

Within the interior of enclosure **32** is provided a suitable protective atmosphere which may be introduced through a conduit **40** and, if necessary, a vent **42** so that a circulating current of such protective atmosphere is present. Depending on the crystal material being produced in the apparatus **10**, the protective atmosphere may comprise a noble gas such as helium or argon, or a reducing gas such as hydrogen or mixtures of hydrogen and nitrogen, or nitrogen alone or mixtures of two or more such gases. In some cases, the space around the crucible may be evacuated to a high vacuum in order to insure the production of crystals free from any gases.

In the event that the process is 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 32 to maintain therein a vapor of such compound at a partial pressure sufficient to prevent impoverishing the melt or the grown crystals with respect to the component. Thus an atmosphere of arsenic may be provided when crystals of gallium arsenide are being pulled. In this case the enclosure 32 also may be suitably heated, for example, by an electrically heated jacket, 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 arsenic thereon.

Under the most ideal conditions for practicing the teachings of this invention, the entire melt 18 would be supercooled. However, this condition is not always obtainable and in some instances only a portion of the melt is supercooled at any one time. The portion of the melt 18 most easily supercooled is that portion directly below the aperture 24 since heat radiating from surface 45 of the melt is dissipated through the aperture instead of being reflected back. It has been found that to produce an elongated body comprised of at least two parallel elongated dendritic crystals crystallographically joined to a unitary body by a thin web or sheet portion extending between the dendritic crystals over the entire length of the body the supercooled portion of the melt must have an area of at least about ¼ square inch on the melt surface 45. If it is attempted to pull the body from a melt having a lesser supercooled surface area, such as 0.12 sq. in., the web or sheet portion of the body will not form.

Referring to FIG. 2 of the drawing there is illustrated, in a greatly enlarged view one type of a seed 126 which may be used with considerable success in accordance with the teachings of this invention to produce the elongated sheet-like body of this invention. The seed 126 is a section of a dendritic crystal which was grown in accordance with the teachings of U.S. patent application Serial No. 844,288, more fully identified hereinabove. It will be understood, of course, that the seed is comprised of the same material as the melt.

The seed 126 as obtained by dendritic growth comprises two relatively flat parallel faces 50 and 52 with three intermediate parallel interior twin planes 54, 55 and 57. Examination will show that the crystallographic structure of the preferred seed on both facs 50 and 52 is that indicated by the crystallographic direction arrows at the right and left faces, respectively, of the figure. It will be noted that the horizontal directions perpendicular to the flat faces 50 and 52 and parallel to the melt surfaces are (111). The direction of growth of the elongated body of this invention will be in a <211> crystallographic direction. If the faces 50 and 52 of the seed 126 were to be etched preferentially to the [111] planes, they will both exhibit equilateral triangular etch pits 58 whose vertices 59 will point upwardly while the bases 60 will be parallel to the surface of the melt. This etch pit orientation will exist for any seed containing a plural odd number of twin planes, and all of such seeds are excellent for the purpose of this invention. Normally the distances between successive twin planes are not the same. A seed containing two twin planes or any even number of twin planes will exhibit triangular etch pits on one face whose vertices will be pointing opposite to the direction of a triangular etch pit on the other face.

The most satisfactory crystal growth is obtained by employing seeds of the type exhibited in FIG. 2, that is, a section of a previously grown dendritic crystal wherein three twin planes are present interiorly and are continuous across the entire cross-section of the seed. It should be understood that the seed need not have flat exterior surfaces 50 and 52, it is only necessary that the (111) planes be parallel to the twin planes. Also, the twin planes need not be exposed at the edges of the seed, as long as they will be exposed to the melt by melting back.

Seed crystals having an odd number (other than 3, that is, 5, 7 and up to 13 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 crystals with their vertices upwardly and the bases parallel to the surface of the melt. Further, seeds containing an even number of twin planes may be employed for crystal pulling, though as desirable pulled bodies will not be obtainable as with the preferred three twin plane seed crystal as shown in FIG. 2. Normally, the pulled body will exhibit the same twin plane structure in the dendritic portion as the seed exhibits.

The direction of withdrawal of the seed having an odd number of twin planes from the melt 18 must be with the direction of the vertices 59 of the etch pits being upwardly and the bases being substantially parallel to the surface of the melt. When so withdrawn, the melt will solidify in indefinitely prolonged growth, at the bottom of the seed in the vertical direction. If the seed 126 were to be inserted into the melt so that the vertices 59 pointed downwardly, very erratic growth will be produced which is not only of non-uniform dimensions but at angles of 120° to the (211) direction and with very irregular spines in the dendritic portion of the body thereby resulting in bodies which are generally unsatisfactory.

When a relatively cold flat seed crystal has been introduced into the melt which is at a temperature at the melting point or only a few degrees above the melting point of the material, the melt will wet and dissolve the tip of the seed and expose the interior twin planes if they do not extend to the surface. There will be a meniscus-like contact area between the seed crystal and the surface of the melt. Such contact area should be maintained throughout the process.

Once good wetting of the seed is obtained and the twin planes are in contact with the melt, the power input to the heating coil is reduced in order to supercool at least that portion of the melt adjacent the seed (or reducing the applied heat if other modes of heat application than RF inductive heating are employed). As illustrated in FIG. 3, there will be observed in a period of time of the order of 5 seconds after the heat input is reduced to the crucible, the supercooling being from 5° C. to 10° C., an initial growth or enlargement 62 which has an elongated hexagonal horizontal cross-section occurs on the surface of the melt attached to the tip of the seed crystal. The hexagonal surface growth increases in area so that in approximately 10 seconds after heat input is reduced its area is approximately 3 times that of the cross section of seed from a dendrite. At this stage, there will be evident spikes 64 and 66 growing at the ends of the hexagonal growth. These spikes appear to grow at the rate of approximately 2 millimeters per second. When the spikes are from two to three millimeters in length and the total length of the hexagonal growth is from about ¼ inch as as much as ¾ inch, the seed crystal pulling mechanism is energized to pull the seed with its attached hexagonal growth from the melt at the desired rate of from ¼ inch to 4 inches per minute and preferably from ¼ inch to 1 inch per minute. If a pull rate of significantly less than ¼ inch per minute is employed the desired crystallographic structure is not obtained. If a pull rate materially greater than 4 inches per minute is used, the web portion of the body will not be formed between the dendrites. The initiation of pulling is timed to the appearance and size of the hexagonal growth with the spikes. After pulling the seed crystal upwardly from the supercooled portion of the melt, it will be observed that from the spikes of the solid hexagonal shaped area portion 62 attached to the seed crystal 126 there are downwardly extending dendrites 68 and 70 formed at each end of the hexagonal area. Accordingly, two parallel dendritic crystals or dendrites are being pulled from the melt at one time from a single seed. These dendrites are parallel to each other and their faces are parallel to the faces of the seed crystal.

When pulled at this critical rate from the melt, a thin web or sheet 72 of solidified material from the melt extends across the space between the two parallel dendrites 68 and 70. The web or sheet 72 is crystallographically joined to the two dendrites 68 and 70, that is, the general crystal structure of the dendrites is continued through the web or sheet 72. However, the web or sheet portion 72 will generally be single crystal material whereas the dendrites will have twin planes extending therethrough. The web usually will have a thickness of at least 0.1 mil, but its thickness will not exceed that of the two dendrites 68 and 70. The web 72 will be substantially dislocation free.

The two dendrites 68 and 70 will remain substantially parallel over the length of the complete elongated body and will thus control the width of the web or sheet portion 72.

The thickness of the web or sheet portion 72 will depend, as pointed out above, to a degree on the thickness of the dendrites 68 and 70, and in addition, by the degree of supercooling of the melt and the pull rate. The higher the degree of supercooling and the slower the pull rate, the thicker the web or sheet portion.

With reference to FIG. 4, there is illustrated a section of the elongated body of FIG. 3 taken along the line IV—IV. This shows how the dendrites 68 and 70 are crystallographically joined to the web or sheet 72. A more detailed description will be given subsequently.

While, as shown in FIG. 2, the section of a previously grown dendrite or dendritic crystal is the preferred form of seed to institute growth of the elongated body of this invention, other seed forms have been found satisfactory. For example, and with reference to FIG. 5 there is shown another suitable seed 74. The seed 74 is comprised of two previously grown dendrites 76 and 78 without any web therebetween, which are joined together at one end by a hexagonal portion 80 at spike portions 82 and 84. The seed 74 of FIG. 5 may be obtained by seeding a supercooled melt with a seed of the type illustrated in FIG. 2 and pulling at a rate in excess of 4 inches per minute whereby only the dendrites grow individually and no web or sheet portion forms.

With reference to FIG. 6 there is illustrated another seed 86 which is essentially the structure of FIG. 3 with a web between two parallel dendrites. After a long sheet-like body has been pulled, the portion 86 shown in FIG. 6 is severed at 88 and used as a seed to initiate further growth. This seed 86 can be used over and over again for initiating satisfactory growth of a successive series of elongated bodies comprised of at least two parallel elongated dendritic crystals crystallographically joined into a unitary body by a thin web or sheet portion extending between the dendritic crystals over the entire length of the body.

In addition, any complete transverse section cut from a previously grown elongated body prepared in accordance with the teaching of this invention is also satisfactory for seeding. Such a seed 94 is shown in FIG. 7 and is comprised of edge portions comprising dendrites 96 and 98 crystallographically joined by a web or sheet portion 100.

If a seed such as is shown in FIG. 5 comprised of double dendritic crystals attached to the original seed is introduced into the same or another melt at or slightly above the melting temperature and after supercooling the melt, on pulling the double dendritic crystal from the surface, there will be formed two separate hexagonal shaped areas attached to each of the dendrites and four dendritic crystals will be pulled—two attached to each of the original dendrites. The area between each of the adjacent dendrites will, in accordance with the teachings of this invention, be filled in with a web or sheet portion. The resulting body, a fragmentary view of which is shown in FIG. 8, will be comprised of four dendrites 102, 104, 106 and 108 crystallographically joined by web or sheet portions 110, 112 and 114 respectively disposed therebetween. Sheet-like bodies with three dendrites and two web portions also have been obtained.

A body of the material prepared in accordance with the teachings of this invention may vary from less than one inch to many feet in length. The width may be up to one inch with three or more parallel dendrites, and up to ¾ inch for two dendrites. The web portion has been obtained in widths of ½ inch and more. Segments or sections of any desired length can be cut from the grown or pulled elongated bodies by sand blasting, fracturing, or electron beam cutting, or by any other similar process known to those skilled in the art.

The body prepared in accordance with the teachings of this invention is comprised of at least two dendritic crystals, at the edges, which extend the entire length of the body, crystallographically joined by a web or sheet portion over their entire length.

The dendritic portions of the body of material will be comprised of dendritic crystals having two highly parallel flat faces which may comprise a series of flat portions differing by steps of about 50 angstroms from each other. The dendritic portions will have a thickness of from approximately two to 25 mils and the width across the flat faces may be from 20 mils to 200 mils and even wider. The surface of the flat faces will exhibit essentially perfect 111 orientation. The dendritic crystals will contain two or more twin planes which will usually extend the entire length of the dendritic crystal and will be parallel to the two parallel flat faces. In addition, the dendritic portions of the body will be of substantially uniform thickness over the entire length of the body, at the extreme not varying as much as 0.1 mil in length of over 12 inches. A more detailed description of the dendritic portion of the bodies of this invention will be found in U.S. patent application Serial No. 844,288. The dendrites set forth in this patent application are essentially identical to the dendritic portion of the body of this invention.

The web or sheet portions of the body crystallographically joins the two or more dendritic crystals which comprise the dendritic portion of the body, and extends the entire length of the body.

The web or sheet portion will have a thickness of at least approximately 0.1 mil, usually from 0.3 to 0.5 mils to 1 mil. The web portion normally will be much thinner than the dendritic crystal between which it is disposed. Also the web portion will be more uniform than the dendrite portions.

The surfaces of the web or sheet portion will be substantially parallel and will approximate very closely the 111 planes. Examination by optical and interference microscopy shows the surfaces to be extremely smooth in nearly all cases when grown properly. However, in some cases the surfaces will be smooth in the central part but will contain reverse steps on other parts especially in the area near the dendrite portions. The height of these steps when present are generally no more than 300 angstroms.

The web or sheet portions of the bodies of this invention are substantially dislocation free and silicon bodies have been prepared having less than 450 dislocations per square centimeters.

The internal structure of the web or sheet portion falls into three classes and these are illustrated in FIGS. 9, 10 and 11.

The most common, and preferred, internal structure of the web or sheet portion is the single crystal structure. With reference to FIG. 9, when web or sheet portion **116** is single crystal, all twin planes, for example twin planes **118**, **120** and **122** are present only in and terminate at the edge of the dendrites **124** and **128** disposed on each side of the web or sheet portion **116**. The twin planes do not extend into the web portion. In this configuration, the twin plane structure in the dendritic portion on each side of the web or sheet is asymmetric with respect to the web, that is, it does not extend entirely across the width of the dendrite, the web or sheet portion will be single crystal.

With reference to FIG. 10, in some cases at least one twin plane, for example, twin plane **130** will extend across both dendrites **132** and **134** and through web or sheet portion **136**. Since, relative to electrical properties, material containing twin planes behaves essentially the same as single crystal material, the fact that at least one twin plane extends across the web or sheet portion does not detract from the usability of the material for the fabrication of electrical devices, especially semiconductor devices such as transistors, diodes, solar cells and the like.

Occasionally, there is found the configuration shown in FIG. 11, in which is illustrated a body of material in which twin planes **140** and **142** originating in dendritic portions **144** and **146** respectively, are mismatched and form an incoherent twin boundary **148** within the web or sheet portion **150**. Such bodies are less desirable than those shown in FIGS. 9 and 10, but are still suitable for use in fabrication of certain semiconductor devices.

The internal structure of the web or sheet portions of the body of material of this invention is controlled or at least influenced by (1) the twin structure of the dendritic portions on each side of the sheet, (2) the thickness of the web or sheet, and (3) thermal distribution in the melt.

When the process is carried out to produce the thinner web or sheet portions, for example, webs of from 0.3 mil to 3 mils, these will normally be single crystal because the twin planes will be asymmetric with respect thereto at the edge of the dendritic portion of the body and therefore the twin planes do not extend into the thin sheet. The growth of single crystal web portions can be assured by using seeds wherein the twin planes are closer to one surface of the seed than the other.

The elongated sheet like bodies comprised of at least two parallel elongated dendritic crystals crystallographically joined to a unitary body by a thin web or sheet portion extending between the dendritic crystals over the entire length of the body of the present invention are relatively flexible and may be bent on a circle of a radius of about 4 inches or even less without breaking. Consequently, crystals may be continuously drawn from the melt and wound on a cylinder of a radius of this order or greater in continuous lengths as desired. The thinner the body the smaller the radius of the coil that may be made therefrom.

The bodies of material grown in accordance with the teachings of this invention have surfaces both on the dendritic portion and on the web portion of such perfection that in the case of semiconductive materials they may be employed for fabricating semiconductor devices simply by applying to the surfaces desired alloys or solders without any intermediate polishing, lapping or etching. In fact, in general, etching results in a degradation of the perfection of the crystal surfaces. In all cases the dendritic portion surface has a perfect 111 orientation as grown and the web or sheet portion have surfaces that very closely approximate 111 planes. In the making of semiconductor devices such as diodes, transistors, photodiodes and other similar semiconductor devices, the 111 surface is a particularly desirable orientation.

The elongated body of this invention may be grown in an intrinsic form from a melt free of doping impurities, or the bodies may be grown doped to a specific type of

semiconductivity and resistivity from a melt containing either acceptor or donor impurities. Examples of acceptor impurities include aluminum, boron, gallium, and indium. Examples of donor impurities include phosphorus, arsenic, and antimony.

One noticeable advantage obtained in practicing the present invention is that, while the previously known processes for growing crystals by the Czochralski technique result in a crystal in which the proportions of the doping impurities are usually radically different from the proportions of the doping impurities in the melt, it has been found in general the proportion of doping impurities in the pulled crystalline bodies of this invention will be much closer to the proportions in the melt using the process of this invention.

As a result of doping, sheet-like bodies of silicon have been prepared in accordance with the teachings of this invention having resistivities varying from less than 0.01 ohm-cm. to greater than 200 ohm-cm. Pure silicon bodies with higher resistivities have also been obtained.

The elongated bodies of this invention and prepared in accordance with the teachings of this invention, provided an excellent material for the efficient and economical fabrication of semiconductor devices such as transistors, diodes, two and three terminal four region devices, solar cells and related devices. Transistors have been prepared from silicon bodies prepared in accordance with the teachings of this invention and have been found to have a gain (beta) of at least 50. In addition, solar cells having an efficiency of from 10 to 15% have been made on silicon bodies grown in accordance with the teachings of this invention.

When fabricating semiconductor devices prepared in accordance with the teachings of this invention, the edge dendritic portions can be left on the bodies or they may be removed by sand blasting, electron beam cutting, chemical etching or the like and the device fabricated entirely upon the single crystal web or sheet portion of the body.

The following examples are illustrative of the practice of this invention:

Example I

An elongated body was prepared in accordance with the teachings of this invention in the following manner.

In apparatus similar to FIG. 1, a quartz lined graphite crucible containing a quantity of intrinsic silicon is heated by the induction coil to a temperature a few degrees above the melting point of silicon, the temperature being about 1430° C., until the entire quantity forms a molten pool. A seed comprising a section cut from a previously grown dendrite and having three interior twin planes extending entirely therethrough and oriented as in FIG. 2 of the drawings, that is, with the etch pit vertices directed upwardly, is held vertically in a holder and is lowered until its lower end touches the surface of the molten silicon. The contact with the molten silicon is maintained until a small portion of the end of the dendritic seed crystal is thoroughly wetted and is melted. Thereafter, the temperature of the melt is lowered rapidly in a matter of 5 seconds by reducing current to the coil **20**, to a temperature 8° C. below the melting point of the silicon so that the melt is supercooled (temperature about 1419° C.). After an interval of approximately 10 seconds at this temperature until an elongated hexagonal portion about ¼ inch long formed, the seed crystal is pulled upwardly at the rate of 1 inch per minute from the supercooled portion of the melt which supercooled portion has a surface area of approximately ¼ sq. inch. Two dendritic crystals were attached to the spiked ends of the hexagonal portion attached to the seed and each was of a thickness of 25 mils and was approximately 30 mils in width. The outside edges of the dendrite portions were approximately 0.25 inch apart. A sloping portion of about 20 mils extended inwardly to a central web portion of a width of about 150 mils. The grown dendritic crystal edge portions has substantially flat and parallel faces from end to end with (111) orientation.

The two dendrite portions were crystallographically joined by a single crystal thin web having a thickness of approximately 3 mils. The surfaces of the web portion very closely approximated (111) planes.

The body as grown was comprised of two dendrite portions crystallographically joined along their entire length by the web or sheet portion. The body was grown to a length of about 14 inches and is shown schematically in FIG. 12 with the major dimensions set forth.

The dentritic portions of the body were found to have no visual microscopic surface imperfections except for a number of microscopic steps differing by about 50 angstroms. The web or sheet portion was found to have essentially flat surfaces over the entire length of the body and to be highly dislocation free.

In a similar manner sheet-like bodies are produced using a germanium seed having three twin planes. These bodies have dendritic edge portions and single crystal web portions having a thickness of 0.3 mil extending therebetween. Likewise, webbed dendritic bodies may be prepared from gallium arsenide and other III–V compounds.

Example II

The procedure of Example I was repeated except that the pull rate was increased to 3 inches per minute and the melt comprised of silicon was doped with two parts per billion of boron.

The resulting sheet-like body resembled that of Example I, except the web portion was thinner, and had a p-type semiconductivity and a resistivity of 200 ohms-cm.

Example III

The procedure of Example I was repeated except that the pull rate was increased to 4 inches per minute and the melt comprised of 35 grams of silicon was doped with .00067 gram of arsenic.

The resulting body was similar to that of Example I, the web being thinner, and the dendritic portions were 7 mils thick, had n-type semiconductivity, and a resistivity of 0.1 ohm-cm.

Example IV

The procedure of Example I was repeated except that a pull rate of 2 inches per minute was used and a seed comprised of 2 dendrites was employed as is illustrated in FIG. 5. The resultant body was comprised of four elongated dentrites joined by a web or sheet portion disposed between adjacent dentrites. The body had the configuration shown in FIG. 8 of the drawings. Each dendritic portion had a width of 7 mils and a thickness of about 20 mils. The web portions were about 70 mils wide and 4 mils thick.

Example V

The procedure of Example I was repeated except that the surface area of the supercooled melt was limited to ⅛ sq. inch. The dendritic growth was observed but there was no web or sheet portion between the two dendrites.

It will be understood that while it is a preferred embodiment of this invention to produce elongated bodies having flat surfaced portions of (111) orientation disposed between at least two dendrites, the flat surface portions can also be grown with (110) or (100) surface orientation. It is also possible to grow the elongated bodies of this invention by pulling properly oriented seeds from the melt in the <110> and <100> directions.

Since certain changes in carrying out the above process and in the product embodying the invention may be made without departing from its scope, it is intended that the accompanying description and drawings be interpreted as illustrative and not limiting.

We claim as our invention:

1. An elongated body of semiconductor material crystallizing in the diamond cubic lattice structure comprised of at least two parallel elongated dendritic crystal portions, each dendritic portion consisting of a dendritic crystal having a plurality of twin planes and a thin web portion therebetween, said thin web portion having substantially parallel flat faces and being substantially dislocation free, said dendritic crystals being joined crystallographically into a unitary body by the thin web portion of the same semiconductor material extending between the dendritic crystals over the entire length of the body.

2. An elongated body of a semiconductor material crystallizing in the diamond cubic lattice structure comprised of at least two parallel elongated dendritic crystals and a thin web portion therebetween, said dendritic crystals being joined crystallographically into a unitary body by the thin web portion of the same semiconductor material extending between the dendritic crystals over the length of the body and a plurality of twin planes extending only through the dendritic crystals over their entire length.

3. An elongated body of a semiconductor material crystallizing in the diamond cubic lattice structure comprised of at least two parallel elongated dendritic crystal portions, each dendritic portion consisting of a dendritic crystal having a plurality of twin planes, said dendritic crystal portions being joined crystallographically into a unitary body by a thin web portion of the same semiconductor material extending between the dendritic crystal portion over the length of the body, the plurality of twin planes extending through the dendritic crystals and at least some of the twin planes extending through the web portion.

4. An elongated unitary body of a semiconductor material comprising a central portion and two edge portions extending the full length of the body, said central portions being comprised of single crystal semiconductor material crystallographically joined to the edge portions, and each of said edge portions being comprised of a dendritic crystal of a semiconductor material, said dendritic crystal containing a plurality of twin planes.

5. An elongated unitary body of a semiconductor material comprising a central portion and two edge portions extending the full length of the body, said central portion being comprised of a thin flat sheet of substantially dislocation free single crystal semiconductor material crystallographically joined to the edge portions, and each of said edge portions being comprised of a dendritic crystal of a semiconductor material, said dendritic crystal containing a plurality of twin planes.

6. An elongated unitary body of a semiconductor material comprising a central portion and two edge portions, said central portion being comprised of a thin flat sheet of substantially dislocation free single crystal semiconductor material crystallographically joined to the edge portions, and each of said edge portions being comprised of a dendritic crystal of the semiconductor material, said dendritic crystal containing a plurality of twin planes, said central portion having a substantially uniform thickness over the length of the body, and said edge portions being substantially uniformly spaced over the length of the body.

7. A pulled substantially planar unitary body of a material crystallizing in the diamond cubic lattice structure, the body comprising two parallel edges comprised of a dendritic crystal having twin planes therein and a central portion joined to the entire length of each of the edges, the central portion consisting of at least one area of single crystal material extending parallel to the edges.

8. A pulled unitary body of a material crystallizing in the diamond cubic lattice structure, the body comprising two parallel edge portions, each edge portion comprising a dendritic crystal having twin planes therein, and a central portion joined to the entire length of at least one of the edge portions, the central portion consisting of at least one flat area of single crystal material of a thickness substantially less than the thickness of the dendritic edge portions, the flat area extending parallel to the edges.

9. An elongated unitary body of a semiconductor material crystallizing in the diamond cubic lattice structure selected from the group consisting of silicon, germanium and stoichiometric compounds having an average of 4 valance electrons per atom, said body being comprised of a central portion and two edge portions, said central portion being comprised of a flat substantially dislocation free single crystal sheet having a substantially uniform thickness throughout the length of the body of at least approximately 0.1 mil, said central portion being crystallographically joined to said edge portions, and each of said edge portions being comprised of a dendritic crystal, said dendritic crystal containing a plurality of twin planes, said edge portions being substantially uniformly spaced over the length of the body.

10. An elongated unitary body of a semiconductor material crystallizing in the diamond cubic lattice structure selected from the group consisting of silicon, germanium and stoichiometric compounds having an average of 4 valance electrons per atom, said body being comprised of a central portion and two edge portions, said central portion being comprised of a flat substantially dislocation free single crystal sheet having a substantially uniform thickness throughout the length of the body of at least one mil, and each of said edge portions being comprised of a dendritic crystal having a thickness greater than the sheet, each of said dendritic edge portions having a plurality of interior twin planes extending entirely therethrough, and two flat exterior surfaces parallel to the twin planes and substantially parallel to the single crystal sheet, the surfaces of the dendrites having essentially perfect (111) orientation.

11. An elongated unitary body of silicon, said body being comprised of a central portion of a flat substantially dislocation free single crystal sheet having a substantially uniform thickness throughout the length of the body of at least approximately 0.5 mil, and two edge portions, each of said edge portions being comprised of a dendritic crystal having a thickness greater than the sheet, each of said dendritic edge portions having a plurality of interior twin planes extending entirely therethrough, and two flat exterior surfaces parallel to the twin planes and substantially parallel to the single crystal sheet, the surfaces of the dendrites having essentially perfect (111) orientation.

12. A substantially planar elongated unitary body of a semiconductor material comprising a plurality of substantially parallel spaced dendritic crystals of a semiconductor material crystallizing in the diamond cubic lattice structure consisting of silicon, germanium and stoichiometric compounds having an average of 4 valance electrons per atom, each of said dendritic crystals having a plurality of interior twin planes extending entirely therethrough, and two flat exterior surfaces parallel to the twin planes, the surfaces of the dendrites having essentially perfect (111) orientation, adjacent dendrites being crystallographically joined to a thin sheet of a single crystal semiconductor material, the thin sheet being comprised of the same semiconductor material as the dendrites, the sheet having a thickness of less than the adjacent dendrites, and the thickness extending the entire length of the body.

13. A substantially planar elongated unitary body of a semiconductor material comprising a plurality of substantially parallel spaced dendritic crystals of a semiconductor material crystallizing in the diamond cubic lattice structure consisting of silicon, germanium and stoichiometric compounds having an average of 4 valance electrons per atom, each of said dendric crystals having a plurality of interior twin planes extending entirely therethrough, and two flat exterior surfaces parallel to the twin planes, the surfaces of the dentrites having essentially perfect (11) orientation, adjacent dendrites being crystallographically joined by a thin sheet of single crystal semiconductor material, the thin sheet being comprised of the same semiconductor material as the dendrites, the sheet being substantially dislocation free and having a thickness of at least approximately 0.5 mil and being thinner than the adjacent dendrites, and the sheet extending the entire length of the body.

14. An elongated unitary body of silicon comprising a plurality of substantially parallel spaced dendritic crystals, adjacent parallel dendrites being crystallographically joined by a thin sheet of single crystal silicon, the thin sheet being substantially dislocation free and having a thickness of at least at approximately 0.5 mil throughout the length of the elongated body.

15. In the process of producing an elongated body of a material crystallizing in the diamond cubic lattice structure comprised of at least two parallel elongated dendritic crystals, each of said dendritic crystals containing a plurality of twin planes, said dendritic crystals being joined crystallographically into a unitary body by a thin single crystal web portion of the same semiconductor material extending between the dendritic crystals, the steps comprising melting a quantity of the material, bringing the melt to a temperature at approximately the melting point of the material, contacting a surface of the melted material with at least a surface of a seed crystal of the material for a period of time to wet the seed crystal with the melted material, the seed crystal having at least two twin planes extending across at least a portion of the surface in contact with the melt, the seed crystal being oriented with a (111) direction parallel to the surface of the melt and a (211) direction perpendicular to the surface of the melt, the twin planes being parallel to the (211) direction, supercooling at least a portion of the melt to a temperature at least 5° C. below the melting point, the surface area of the supercooled portion being at least 0.25 sq. inch, and pulling the seed crystal from the melt at a rate of approximately ¼ inch per minute to 4 inches per minute, whereby the material from the supercooled portion of the melt solidifies on the seed crystal and on continuous pulling of the seed produces an elongated body comprised of at least two dendritic crystals crystallographically joined by a thin web of material.

16. In the process of producing an elongated body of a material crystallizing in the diamond cubic lattice structure comprised of at least two parallel elongated dendritic crystals, each of said dendritic crystals containing a plurality of twin planes, said dendritic crystal being joined crystallographically into a unitary body by a thin single crystal web portion of the same semiconductor material extending between the dendritic crystals, 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 the melted material with at least a surface of a seed crystal of the material for a period of time to wet the seed crystal with the melted material, the seed crystal having at least two thin planes extending across at least a portion of the surface in contact with the melt, the seed crystal being oriented with a (111) direction parallel to the surface of the melt and a (211) direction perpendicular to the surface of the melt, the twin planes being parallel to the (211) direction, supercooling at least a portion of the melt to a temperature 5° C. to 10° C. below the melting point, the surface area of the supercooled portion being at least 0.25 sq. inch, and pulling the seed crystal from the melt at a rate of approximately ¼ inch to 1 inch per minute whereby the material from the supercooled portion of the melt solidifies on the seed crystal and produces an elongated body comprised of at least two dendritic crystals crystallographically joined by a thin web of material.

17. In the process of producing an elongated body of a material crystallized in the diamond cubic lattice structure comprised of at least two parallel elongated dendritic crystals, each of said dendritic crystals containing a plurality of twin planes, said dendritic crystals being joined

crystallographically into a unitary body by a thin single crystal web portion of the same semiconductor material extending between the dendritic crystals, the steps comprising melting a quantity of the material, bring the melt to a temperature slightly above the melting point of the material, contacting the surface of the melt with at least a surface of a seed crystal of a material for a period of time to wet the seed crystal with the melted material, the seed crystal having at least two twin planes extending across at least a portion of the surface in contact with the melt, the seed crystal being oriented with a (111) direction parallel to the surface of the melt and a (211) direction perpendicular to the surface of the melt, the twin planes being parallel to the (211) direction, supercooling at least a portion of the melt to a temperature 5° C. to 10° C. below the melting point, the surface area of the supercooled portion being at least 0.25 sq inch, and preferably at least 0.75 sq. inch and pulling the seed crystal from the melt to the rate of from approximately ¼ inch per minute to 4 inches per minute whereby the material from the supercooled portion of the melt solidifies on the seed crystal and produces an elongated body comprised of at least two dendritic crystals crystallographically joined by a thin web of the material.

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