



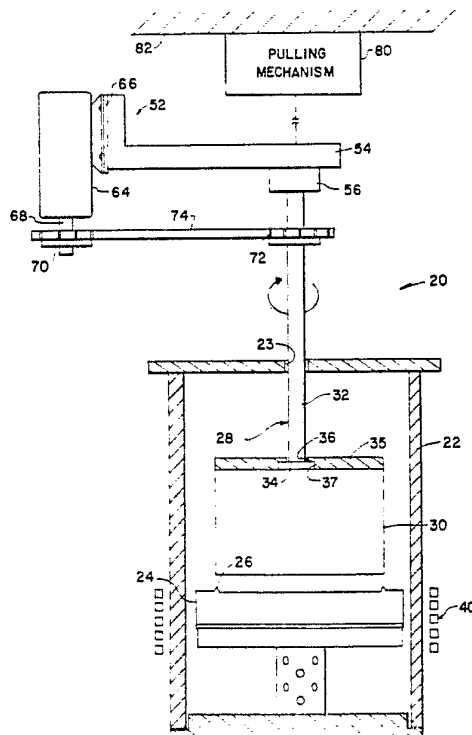
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>5</sup> : <b>B01D 9/00</b></p>	<p><b>A1</b></p>	<p>(11) International Publication Number: <b>WO 92/03204</b> (43) International Publication Date: 5 March 1992 (05.03.92)</p>
<p>(21) International Application Number: PCT/US91/05676 (22) International Filing Date: 9 August 1991 (09.08.91) (30) Priority data: 567,938 15 August 1990 (15.08.90) US (71) Applicant: MOBIL SOLAR ENERGY CORPORATION [US/US]; Middlesex Technology Center, 4 Suburban Park Drive, Billerica, MA 01821 (US). (72) Inventors: KALEJS, Juris, P. ; 54 Northgate Road, Wellesley, MA 02181 (US). STORMONT, Richard, W. ; 40 Sylvia Drive, Warwick, RI 02886 (US).</p>		<p>(74) Agent: PANDISCIO, Nicholas, A.; 125 CambridgePark Drive, Cambridge, MA 02140 (US). (81) Designated States: AU, BE (European patent), CA, CH, CH (European patent), DE, DE (European patent), FR (European patent), GB, GB (European patent), IT (European patent), JP, KR, NL, NL (European patent), SE, SE (European patent). <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>

(54) Title: METHOD OF GROWING CYLINDRICAL TUBULAR CRYSTALLINE BODIES

(57) Abstract

A method of growing cylindrical tubular crystalline bodies having impurities distributed therein at improved levels of uniformity relative to the distribution of impurities in non-cylindrical tubular crystalline bodies which are not rotated during the growth thereof. The method involves forming a cylindrical tubular crystalline body by the EFG process including rotating the crystalline body at about 35-65 rpms the entire time the body is being pulled from the forming die. Crystalline bodies having a wall thickness of 5 mils, plus or minus 0.5 mils have been grown by the method.



**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU <sup>+</sup>	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE <sup>+</sup>	Germany	MC	Monaco	US	United States of America
DK	Denmark				

<sup>+</sup> Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

METHOD OF GROWING CYLINDRICAL TUBULAR  
CRYSTALLINE BODIES

FIELD OF THE INVENTION

This invention pertains to methods of growing crystals, and more particularly to methods of growing cylindrical tubular crystalline bodies by the EFG process.

BACKGROUND OF THE INVENTION

Silicon sheet used in the fabrication of photovoltaic devices is frequently formed from the flat sides of tubular crystalline bodies of the type having a polygonal cross section, e.g., a nonagon crystal. Apparatus of the type described in U.S. Patent No. 4,544,528 have been used to manufacture these crystalline bodies according to the edge-defined, film-fed growth process (the EFG process). Briefly, these apparatus comprise a crucible for containing a melt of the material to be grown (e.g., silicon), a capillary die for controlling the form and shape of the grown crystal, a heater for controlling the temperature of the die and melt, a seed support assembly for supporting the seed used in growing the crystal, and a pulling mechanism coupled to the seed support assembly for drawing the tubular crystalline body out of the melt.

It is also known to grow tubular crystalline bodies with apparatus of the type disclosed in U.S. Patent No. 4,544,528, as set forth in the article "Large Area

-2-

Silicon Sheet Via EFG Tube Growth" by Taylor et al., published in Proceedings of the Fifteenth IEEE Photovoltaic Specialists Conference, June 1981, pages 589-594. Taylor et al. grew tubular crystalline bodies up to 9 cm in diameter, with wall thicknesses ranging from 0.015 to 0.071 cm. The crystalline bodies were not rotated during the growth thereof. It was intended that solar cell substrates would be fabricated by flattening rectangular portions of the wall of the tubular body.

Crystalline bodies grown with the apparatus of U.S. Patent No. 4,544,528 are not rotated about their long axes during the growth thereof. It is known, however, to rotate elongate, hollow crystalline bodies during the growth thereof by the EFG process, as illustrated in U.S. Patent No. 3,846,082 to LaBelle, Jr. et al. and in the article "The Tubular Solar Cell - A New Concept for Photovoltaic Power Generation", by Mlavsky et al., published in Proceedings of the Twelfth IEEE Photovoltaic Specialists Conference, 1976. Crystalline bodies grown by the apparatus of U.S. Patent No. 3,846,082 have spirally-shaped interior and/or exterior surfaces. Unlike the crystalline bodies grown with the apparatus developed by LaBelle Jr. et al., the crystalline bodies grown by Mlavsky et al. were tubular, i.e. they had parallel interior and exterior walls that were substantially straight along the length thereof.

The Mlavsky et al. process for growing a crystalline body involves rotating the body only during

-3-

the initial formation thereof. As soon as the pulling mechanism begins to pull the crystalline body away from the die, rotation of the body is stopped. The tubular bodies grown by Mlavsky et al. were about 0.375 inches in diameter and were mounted whole in the collector of a photovoltaic-solar thermal energy system.

Tubular crystalline bodies grown by the Mlavsky et al. process tend to have one or more regions extending along the length of the body, in which the impurity concentration is much higher than in the remainder of the body. Conventional solar cell substrates cannot be cut from tubular crystalline bodies grown by the Mlavsky et al. process due to the small diameter of the bodies. However, if even crystalline bodies of a suitable diameter could be grown by the process of Mlavsky et al., it is believed that the impurity "rashes" present in the crystalline bodies grown by Mlavsky et al. would render the Mlavsky et al. process unsuitable as a method of growing crystalline bodies from which solar cell substrates could be fabricated. Solar cells made from substrates cut from portions of a crystalline body having these impurity "rashes" tend to be relatively inefficient. As such, a significant portion of a tubular crystalline body grown by the Mlavsky et al. process, assuming a body of suitable diameter could be grown by the Mlavsky et al. process, would in all likelihood not be usable as a substrate material for solar cells.

Apparatus which simultaneously rotate and pull a growing Czochralski-type crystal away from the

-4-

crystalline melt during the entire growth process are also known, as illustrated in U.S. Patent No. 3,552,931 to Doherty et al.

Although satisfactory solar cells have been fabricated using substrates formed from the flat sides of crystalline bodies having a polygonal, e.g., nonagon, cross-section, a desire exists for improving certain properties and characteristics of the crystalline bodies so that improved solar cell substrates can be fabricated therefrom. Specifically, it is desired to produce a hollow crystalline body having improved uniformity of distribution of impurities, as compared to crystalline bodies grown by the above-mentioned apparatus and methods employing the EFG process. By improving the uniformity of distribution of impurities in a crystalline body, dislocation density can be reduced, minority carrier diffusion lengths can be increased, and cell wall thickness can be decreased and can be more precisely controlled.

Additionally, it is desirable to produce a hollow crystalline body having such improved evenness of distribution of impurities which also has a circular cross section.

It is believed that none of the aforementioned apparatus or methods can be used to grow a hollow crystalline body by the EFG process having the desired uniformity of distribution of impurities.

#### OBJECTS AND SUMMARY OF THE INVENTION

-5-

A primary object of the present invention is to provide a method of growing by the EFG process tubular crystalline bodies having parallel cylindrical interior and exterior surfaces and improved uniformity of distribution of the impurities disposed therein as compared to the uniformity of distribution of impurities in a tubular crystalline body of polygonal cross-section grown by the EFG process.

Another object of the present invention is to provide a method of growing by the EFG process tubular cylindrical crystalline bodies having thinner walls, reduced dislocation density and increased minority carrier diffusion lengths, as compared to tubular crystalline bodies of polygonal cross-section grown by the EFG process using known apparatus and methods.

Yet another object of the present invention is to provide a solar cell substrate having improved microstructural characteristics, as compared to solar cell substrates fabricated from crystalline bodies grown by known processes.

These and other objects are achieved by a method of growing by the EFG process tubular cylindrical crystalline bodies having an improved evenness of distribution of impurities relative to tubular crystalline bodies of polygonal cross-section grown by the EFG process without rotation using known apparatus or methods. The method is accomplished using an apparatus comprising a crucible for containing a melt of the material. e.g., silicon, from which the crystalline body is grown, a heater for maintaining the

-6-

melt at selected temperature, a die for forming and determining the shape of the crystalline body, a seed, a seed holder, a pulling mechanism coupleable to the seed holder for pulling the crystalline body away from the die, and a rotation mechanism coupled to the pulling mechanism for rotating the crystalline body about its growth axis while the body is being pulled away from the die. The method involves rotating the seed holder, seed and crystalline body relative to the die at about 50 revolutions per minute during the entire time the crystalline body is being pulled away from the die. The temperature of the melt, pull speed and other control variables are similar to those used in known methods of growing tubular crystalline bodies of polygonal cross-section by the EFG process.

#### DESCRIPTION OF THE DRAWINGS

For a fuller understanding of the nature and objects of the present invention, reference should be had to the following detailed description taken in connection with the accompanying drawing wherein:

Fig. 1 is a schematic elevation view, partially broken away, of the present invention;

Fig. 2 is a photograph presenting a front elevational view of a portion of a cylindrical tubular crystalline body grown from a melt doped with aluminum, with the upper portion of the body being grown without rotation and the bottom portion of the body being grown with rotation; and

Fig. 3 is a photograph presenting a front

-7-

elevational view of a portion of a cylindrical tubular crystalline body grown from a melt doped with iron and aluminum, with the upper portion of the body being grown without rotation and the bottom portion of the body being grown with rotation.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention is a method of growing cylindrical tubular crystalline bodies by the EFG process from molten silicon. Preferably, although not necessarily, Ethyl silicon of the type manufactured by Ethyl Corporation, Electronic Materials Division, of Baton Rouge, Louisiana, is used as the feed stock for the melt. Ethyl silicon is silicon in a high purity, spherical, free-flowing particulate form. It has (1) a particle size distribution ranging from 150 to 1500 microns, with a typical average size of 700 microns, (2) a particle density ranging from 2.25 to 2.33 g/cc, with an average density of 2.30 g/cc, and (3) a bulk density ranging from 1340 to 1380 Kg/m<sup>3</sup>, with an average bulk density of 1360 Kg/m<sup>3</sup>. Ethyl silicon has an average statistical impurity concentration of 0.12 ppba of boron, 0.11 ppba of phosphorous, 0.11 ppba of arsenic, and 0.25 ppma of carbon.

Referring to Fig. 1, the method of the present invention is accomplished using an EFG crystal growing apparatus 20 for growing cylindrical tubular crystalline bodies. The apparatus comprises a furnace enclosure 22 having an aperture 23 extending through the top surface thereof. Apparatus 20 includes

-8-

crucible 24, capillary die 26, seed holder 28 and graphite seed 30, all of which are disposed within enclosure 22. Enclosure 22, crucible 24, capillary die 26, seed holder 28 and graphite seed 30 are substantially identical to the corresponding elements in the crystal forming device disclosed in U.S. Patent No. 4,544,528 (the '528 patent), which is incorporated herein by reference. Attention is directed to this patent for a more detailed description of the structure and function of elements 22-30 of the present invention.

As those of ordinary skill in the art will of course appreciate, the capillary die 26 has a circular cross-sectional configuration (since cylindrical crystalline bodies are grown by the present apparatus) rather than the nonagon cross-sectional configuration of the capillary die of the crystal growing apparatus of the '528 patent. Preferably, die 26 has a diameter selected so that crystalline bodies grown therefrom have an outside diameter ranging about 10 to 30 cm, with smaller and larger diameter dies also being within the scope of the present invention. In other respects capillary die 26 is substantially identical to the capillary die of the '528 patent.

Seed holder 28 comprises an elongate shaft 32 having a flat, circular stop plate 34 secured to the lower end thereof. Seed holder 28 also comprises a top plate 35 having a central bore 36 extending therethrough. The bottom end of bore 36 comprises a counterbore 37. Stop plate 34 is positioned in

-9-

counterbore 37 of top plate 35, and seed 30 attached thereto, hang down from the stop plate. Stop plate 34 and counterbore 37 are sized so that the peripheral edge of stop plate 34 frictionally engages the sidewall of counterbore 37 such that top plate 35 rotates with stop plate 34 and shaft 32 attached thereto, except when a sufficient resistive force is applied to top plate 35. Such a resistive force is generated when, for instance, the growing crystal freezes to the die. When such a resistive force is applied to top plate 35, stop plate 34 will rotate within counterbore 37. This slip-fit connection is provided so that the growing crystal does not shatter in the event of a freeze-up.

Furnace enclosure 22 is surrounded by a heating coil 44 which is coupled to a controllable power supply (not shown) of conventional construction. Heating coil 44 is provided for maintaining the melt supported within crucible 24 at a predetermined temperature. Heating coil 44 is substantially identical to and functions in the same manner as the heating coil surrounding the furnace enclosure of the crystal-growing apparatus disclosed in the '528 patent.

Apparatus 20 further comprises a rotation mechanism 52 coupled with shaft 32 for imparting rotational movement to the latter. Rotation mechanism 52 includes support arm 54 and bearing assembly 56 attached to the underside of one end of the support arm. Bearing assembly 56 is adapted to receive the upper end of shaft 32 and to rotatably support the shaft and prevent the shaft from moving radially or axially relative to

support arm 54.

Rotation mechanism 52 further comprises rotational drive motor 64 which is attached via bracket 66 to the opposite end of support arm 54. Rotational drive motor 64 has an output shaft 68 to which a drive sprocket 70 is attached. A similar driven sprocket 72 is attached to shaft 32 substantially in alignment with drive sprocket 70. Sprockets 70 and 72 are rotationally coupled by a flexible endless drive member 74. Preferably, member 74 is a flexible chain and sprockets 70 and 72 are suitably toothed to engage the chain so that rotational drive can be transmitted from drive sprocket 70 to driven sprocket 72. Alternatively, member 74 may be a flexible V-belt and sprockets 70 and 72 may have a circumferential groove for receiving the V-belt.

Apparatus 20 also comprises a pulling mechanism 80 coupled to rotation mechanism 52 and attached to a fixed surface 82 above the apparatus 20. Pulling mechanism 80 is substantially identical to the pulling mechanism disclosed in U.S. Patent No. 4,544,528. Pulling mechanism 80 is coupled to rotation mechanism 52 so that upon actuation of the former the entire rotation mechanism, as well as seed holder 28 which is attached to the rotation mechanism, will be pulled away from die 26.

Heating coil 44, rotation mechanism 52 and pulling mechanism 80 may be individually operated so as to achieve the operating characteristics required to grow a cylindrical tubular crystalline body with apparatus

-11-

20. Alternatively, heating coil 44, rotation mechanism 52 and pulling mechanism 80 may be coupled to a conventional control unit (not shown) which automatically controls these elements 44, 52 and 80 so as to achieve the operating characteristics required to grow a cylindrical tubular crystalline body with apparatus 20.

To grow a cylindrical tubular crystalline body having parallel cylindrical interior and exterior surfaces according to the method of the present invention, pulling mechanism 80 is operated to lower rotation mechanism 52, and seed holder 28 and seed 30 attached to the rotation mechanism, so that seed 30 will just contact the end face of die 26. Apparatus 20 is now in condition to grow a cylindrical tubular crystalline body.

Heating coil 44 is operated to heat die 26 above the melting point of seed 30 to cause the portion of the latter contacting the die to melt so as to wet the die. Pulling mechanism 80 is now activated to raise rotation mechanism 52, and seed holder 28 and seed 30 attached thereto, away from die 26. As seed 30 rises from the die, the melted seed material wetting the die is drawn out, by surface tension, into a thin film between the seed and the die end face. The previously charged melt of Ethyl silicon in crucible 24 rises, by capillary action, to replenish the material wetting the die end face. The portion of liquid film nearest seed 30 is at a lower temperature than that at the end face of die 32, and begins to solidify as its temperature

-12-

comes below the melting point thereof. Pulling mechanism 80 is operated so as to continue to pull seed 30 away from die 26 until a cylindrical, tubular crystalline body of suitable length hangs from the seed. Pulling mechanism 80 is operated so as to pull seed 30 away from die 26 at substantially the same rate of speed as that of the pulling mechanism of the device of U.S. Patent No. 4,544,528, i.e. about 2.5 cm/min. Pull speed may be satisfactorily controlled using apparatus of the type disclosed in U.S. Patent No. 4,267,151 to Yates et al.

Shortly after a complete meniscus forms around the perimeter of die 26, i.e. typically just after pulling mechanism 80 is first actuated to pull seed 30 away from die 26, rotation mechanism 52 is actuated so as to rotate seed 30 relative to die 26. More specifically, rotational drive motor 64 is actuated causing its output shaft 68 and drive sprocket 70 attached thereto to rotate. This rotation is transmitted via chain or belt 74 to driven sprocket 72. The latter, via its coupling with shaft 32, transmits rotational drive to the shaft. As shaft 32 and stop plate 34 attached thereto rotate, rotational drive is transmitted to top plate 35, seed 30 and the growing crystalline body attached to the seed by virtue of the frictional engagement of stop plate 34 with the sidewall of counterbore 37. Rotational drive motor 64 is preferably operated so that its output shaft 68 rotates at about 35-65, preferably about 50, rotations per minute, although higher rates of rotation, e.g. 100-200

-13-

rpms, may be used if apparatus 20 comprises sufficient mechanical vibrational dampening to prevent breakage or irregular formation of the growing crystalline body.

#### First Example

Referring to Figs. 1 and 2, a hollow tubular crystalline body 100 (Fig. 2) having a circular cross section was grown using crystal growing apparatus 20. Ethyl silicon, as described above, was used as the feed material. After being converted to a molten state in crucible 24 of apparatus 20, the Ethyl silicon was doped with aluminum to a concentration of about 400ppm.

Crystalline body 100 was then grown following the method described above, except that the upper portion 100a (i.e., the first grown portion) of body 100 was grown without rotation. After the growing crystalline body 100 reached a predetermined length, rotation mechanism 52 was activated with the result that the lower portion 100b of the crystalline body was rotated during the growth thereof at a speed of 48 revolutions per minute. Line 102 in Fig. 2 indicates the interface of the non-rotated and rotated portions of crystalline body 100.

As expected, a high-impurity concentration region 104 was formed in the upper portion 100a during the growth thereof. The region 104 was characterized by vertical striations or rashes extending parallel to the axis of the crystalline body 100 and extending across about a 15° segment of the entire circumference of the body. The portions 106 of the upper portion 100a

-14-

adjacent region 104 did not contain such striations. Using conventional atomic absorption spectroscopy, the aluminum impurity concentration of region 104 was determined to be 846 ppm and the aluminum impurity concentration of region 106 was found to be 59ppm.

By way of comparison, the aluminum impurity concentration of region 108 in lower portion 100b, which is positioned directly below region 104 in upper portion 100a, was found to be 506ppm. The aluminum impurity concentration of region 110 adjacent region 108 was found to be 425ppm.

This change in impurity concentration between upper portion 100a and lower portion 100b confirms that the method of the present invention improves the evenness of distribution of impurities in a crystalline body grown according to the method of the present invention.

The melt used to grow crystalline body 100 was doped with aluminum to a much greater concentration than is typical for a melt from which crystalline bodies used to make solar cell substrates are grown. However, it is believed that similar improvement in the uniformity of distribution of impurities will be achieved with the method of the present invention for crystalline bodies grown from a silicon melt having an impurity mix and concentration consistent with that used to grow crystalline bodies from which solar cell substrates are fabricated.

Moreover, for relatively long (e.g., 100 feet) crystalline bodies from which solar cell substrates are formed, impurity concentrations may increase

-15-

precipitously at the end of the growth run, particularly when feedstock having a higher impurity concentration than that of ethyl silicon is used. As such, even for crystalline bodies grown from a silicon melt having a relatively low impurity concentration, the method of the present invention has important application as a process for improving the evenness of distribution of impurities in a crystalline body.

The wall thickness of crystalline body 100 was 5 mils, plus or minus 0.5 mils. By way of comparison, tubular crystalline bodies having a polygonal cross section grown by the EFG process without rotation using state-of-the art crystal growth apparatus, typically have a wall thickness of 16 mils, plus or minus 8 mils.

#### Second Example

Referring now to Figs. 1 and 3, a second experiment was conducted to verify that the method of the present invention improves the evenness of distribution of impurities in a crystalline body. The second experiment was substantially identical to the first experiment described above, except that both iron and aluminum were added as impurities to the silicon melt from which crystalline body 200 was grown. Thus, upper portion 200a was not rotated, while lower portion 200b was rotated during the growth thereof at a speed of 48 revolutions per minute. Line 202 represents the interface between the upper and lower portions.

Conventional atomic absorption spectroscopy revealed that the present method provided an

-16-

improvement in uniformity of distribution of impurities comparable to that described above with respect to the first example. Specifically, in the upper portion 200a of body 200, a high-impurity concentration region 204 was formed having an impurity concentration of 235ppm for iron and 367 for aluminum. The adjacent low-impurity concentration region 206 in upper portion 200a had an impurity concentration of 7ppm for iron and 4ppm for aluminum.

In contrast, the impurity concentration in region 208 of lower portion 200b of body 200, which lower portion was rotated during the growth thereof, was 118ppm for iron and 162ppm for aluminum. Region 208 is positioned directly below high-impurity region 204 in upper portion 200a. The impurity concentration of region 210, which is adjacent region 208 in lower portion 200b, is 126ppm for iron and 164ppm for aluminum.

As these test results indicate, the uniformity of distribution of both the iron and aluminum impurities in crystalline body 200 was improved for the lower portion 200a thereof which was grown with rotation as compared to the top portion which was grown without rotation.

Again, the wall thickness of crystalline body 200 was 5 mils, plus or minus 0.5 mils.

#### Advantages of the Present Invention

It has been determined that a tubular crystalline body grown by rotating the body relative to the die as

-17-

the body is pulled away from the die improves the uniformity of distribution of impurities in the crystalline body, as illustrated in the foregoing examples. In this connection, it is believed that the convection currents induced in the liquid melt by rotation of the crystalline body cause the impurities in the melt to be more evenly distributed throughout the melt. A number of important advantages are achieved by improving the uniformity of distribution of impurities.

First, it is possible to more precisely control the wall thickness of a crystalline body, having improved uniformity of impurity distribution as measured about a circumference thereof. Specifically, with the apparatus of the present invention, it is possible to grow a tubular crystalline body having wall thickness variations of less than  $\pm 0.5$  mils as measured about a selected circumferential band of the body. With the ability to more precisely control wall thickness comes the ability to grow crystalline bodies with the present method having relatively thin walls, e.g. about 5 mils thick.

It is advantageous for a number of reasons to grow crystalline bodies having thinner walls than are ordinarily obtainable with conventional apparatus of the type disclosed in the aforementioned '528 patent in which the crystalline body is not rotated during the growth thereof. Less silicon is required to grow a thin-walled crystalline body, which in turn reduces the cost of producing such a body and solar cell substrates

-18-

made therefrom. Because the cost of silicon is a dominant cost factor in the fabrication of solar cells, by conserving silicon the total cost of producing a solar cell can be reduced. Producing relatively thin-walled crystalline bodies is also advantageous in the ongoing attempt to improve solar cell efficiency. Specifically, a relatively thin substrate is required to produce the relatively highly efficient back surface field effect solar cell. Such a substrate can be satisfactorily produced from a crystalline body grown using the method of the present invention.

A second advantage occurs in connection with improving the uniformity of impurity distribution. Substrates cut from tubular crystalline bodies grown with the apparatus of the present invention have reduced dislocation density and greater as-grown minority carrier diffusion lengths. As is well known, solar cell performance typically decreases as dislocation density increases and increases as minority carrier diffusion lengths increase.

The method of the present invention is also advantageous inasmuch as the crystalline bodies grown according to the method have a circular cross section. As compared to crystalline bodies having polygon cross sections, crystalline bodies having circular cross sections have fewer internal stresses and hence less propensity to crack.

Although it is preferred that Ethyl silicon be used as the feed stock in the present method, the above-described advantages of the present invention are

-19-

also achieved when other, lower grade silicon stock is used.

Since certain changes may be made in the above processes without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted in an illustrative and not limiting sense.

As used in the following claims, "Ethyl silicon" shall mean silicon of the type manufactured by Ethyl Corporation, Electronic Materials Division, of Baton Rouge, Louisiana and described above in greater detail.

What Is Claimed Is:

1. A method of growing a hollow, relatively thin-walled, tubular crystalline body having a circular cross section and an outside diameter sufficient to permit conventional solar cell substrates to be cut from said body, said body being grown from a melt of silicon with an EFG growth apparatus of the type including a crucible for containing said melt, heating means for heating said melt in said crucible, growing means for growing a tubular crystalline body from said melt, said growing means comprising: (1) forming means in said crucible communicating with said melt for controlling the shape of said crystalline body so that the latter is of sufficient diameter to permit a plurality of relatively thin conventional solar cells substrates to be cut from said body, (2) seed holder means for supporting a seed onto which said crystalline body is grown, (3) pulling means for pulling said tubular crystalline body, said seed, and said seed holder means away from said forming means, and (4) rotating means for rotating said tubular crystalline body, said seed and said seed holder relative to said forming means, the method comprising:

providing a melt of silicon in said crucible, said melt having impurities therein;

operating said apparatus so as to commence growing a tubular crystalline body out of said melt;

pulling said tubular crystalline body, said seed and said seed holder away from said forming means at a

-21-

selected rate of speed; and

rotating said tubular crystalline body, said seed and said seed holder relative to said forming means at a selected rate of rotation during the entire period of time said tubular crystalline body, said seed and said seed holder are being pulled away from said forming means, said rate of rotation being selected (a) so as to ensure said impurities in said melt are substantially evenly distributed about the circumference of said body and (b) so as to substantially prevent the formation of high impurity-concentration rashes in said body.

2. A method according to claim 1 wherein said rate of rotation is chosen so that said wall thickness varies no more than 0.5 mils from a desired wall thickness value, as measured about any circumferential band selected along the length of said body.

3. A method according to claim 1 wherein said rate of rotation ranges from 35-65 revolutions per minute.

4. A method according to claim 3 wherein said selected rate of rotation is about 50 revolutions per minute.

5. A method according to claim 1 wherein said tubular crystalline body has a wall thickness ranging from 4.5 to 5.5 mils.

-22-

6. A method according to claim 1 wherein said melt comprises Ethyl Silicon.

7. A method according to claim 1 wherein said seed is pulled at a rate of about 2.5 cm/min and said rate of rotation is in the range of 35-65 revolutions per minute.

8. A method according to claim 1 wherein said rate of rotation is in the range of 35-200 revolutions per minute.

9. A relatively thin-walled tubular, hollow crystalline silicon body grown according to the method of claim 1.

10. A body according to claim 9 having a wall thickness of 5 mils, plus or minus 0.5 mils.

11. A body according to claim 9 wherein impurities therein are substantially evenly distributed around the circumference thereof, as measured at any location along the length of the body.

12. A method of growing a hollow, relatively thin-walled, tubular crystalline body of silicon having a circular cross section and an outside diameter sufficient to permit conventional solar cell substrates to be cut from said body, said method comprising:

(1) providing an EFG growth apparatus that

-23-

includes a (a) crucible for containing a supply of silicon, (b) heating means for heating said crucible so as to convert a supply of solid silicon in said crucible to a melt, (c) a capillary die having a capillary communicating with the interior of said crucible and an upper end surface for supporting a film of said melt, said upper end surface being configured so that a crystalline body grown from said film of melt will be cylindrical in cross-section and have a diameter sufficient to permit a plurality of relatively thin conventional solar cell substrates to be cut from said body, (d) seed holder means for supporting a seed onto which said crystalline body is grown, (e) pulling means connected to said seed holder means for moving said seed holder means, said seed and a growing crystalline body attached to said seed vertically toward or away from said capillary die, and (f) rotating means for rotating said seed holder, said seed and said growing crystalline body relative to said capillary die and said crucible,

(2) providing a supply of silicon in said crucible and heating said silicon so as to form a melt of silicon in said crucible;

(3) operating said apparatus so that a tubular crystalline body with a circular cross-section commences to grow onto said seed from a film of melt on the upper end of said capillary die;

(4) pulling said seed holder, said seed and said tubular crystalline body vertically away from said capillary die at a selected rate of speed; and

-24-

(5) rotating said seed holder, said seed and said growing tubular crystalline body relative to said capillary die at a selected rate of rotation as said seed holder, seed and growing tubular crystalline body are being pulled away from said capillary die, said rate of rotation being selected so as to (a) ensure that impurities in said melt are substantially evenly distributed about the circumference of said body and (b) substantially prevent the formation of high impurity-concentration rashes in said body.

13. A method according to claim 12 wherein said rate of rotation is chosen so that said wall thickness varies no more than 0.5 mils from a desired wall thickness value, as measured about any circumferential band selected along the length of said body.

14. A method according to claim 12 wherein said seed is pulled at a rate of about 2.5 cm/min and said rate of rotation is in the range of 35-65 revolutions per minute.

15. A method according to claim 12 wherein said rate of rotation is in the range of 35-200 revolutions per minute.

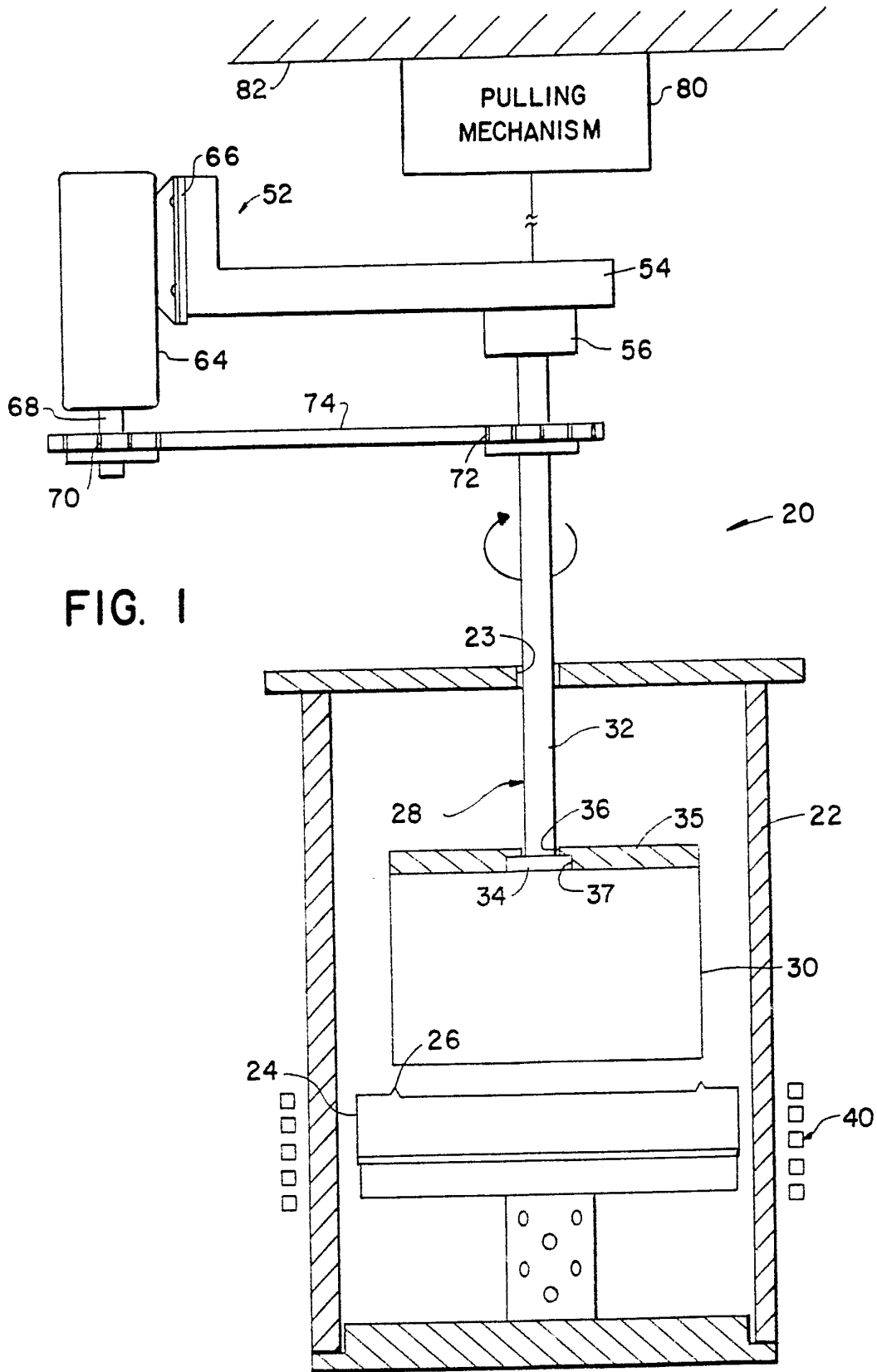


FIG. 1

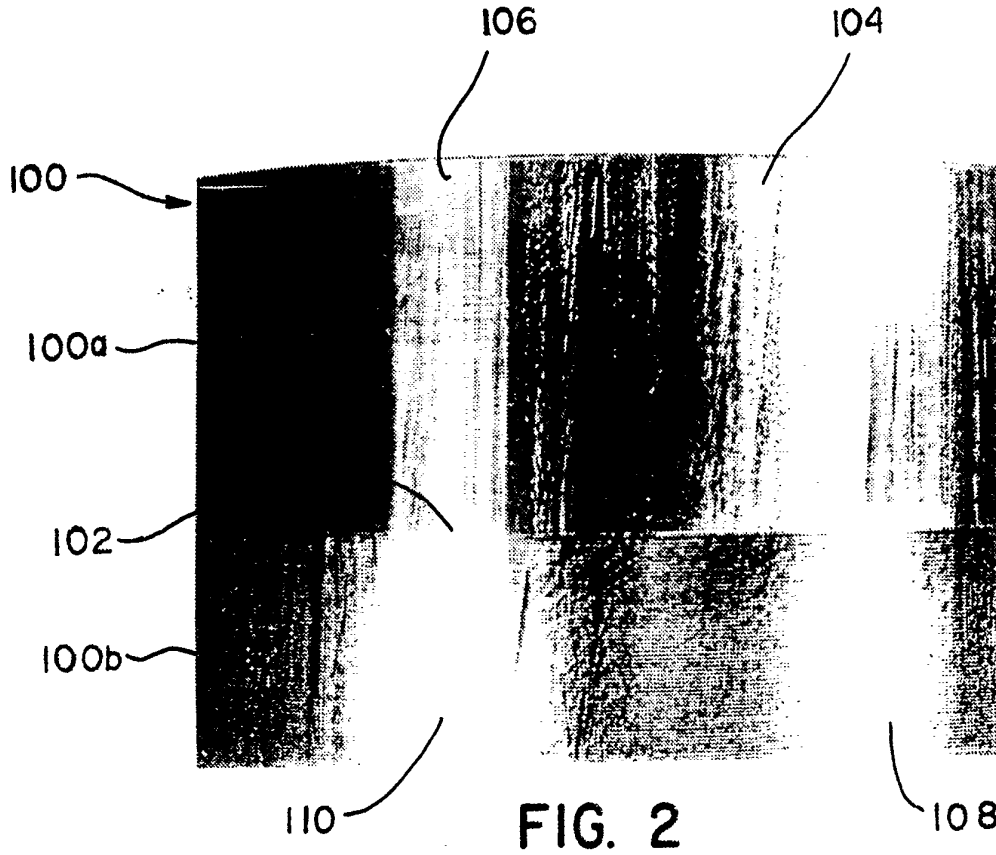


FIG. 2

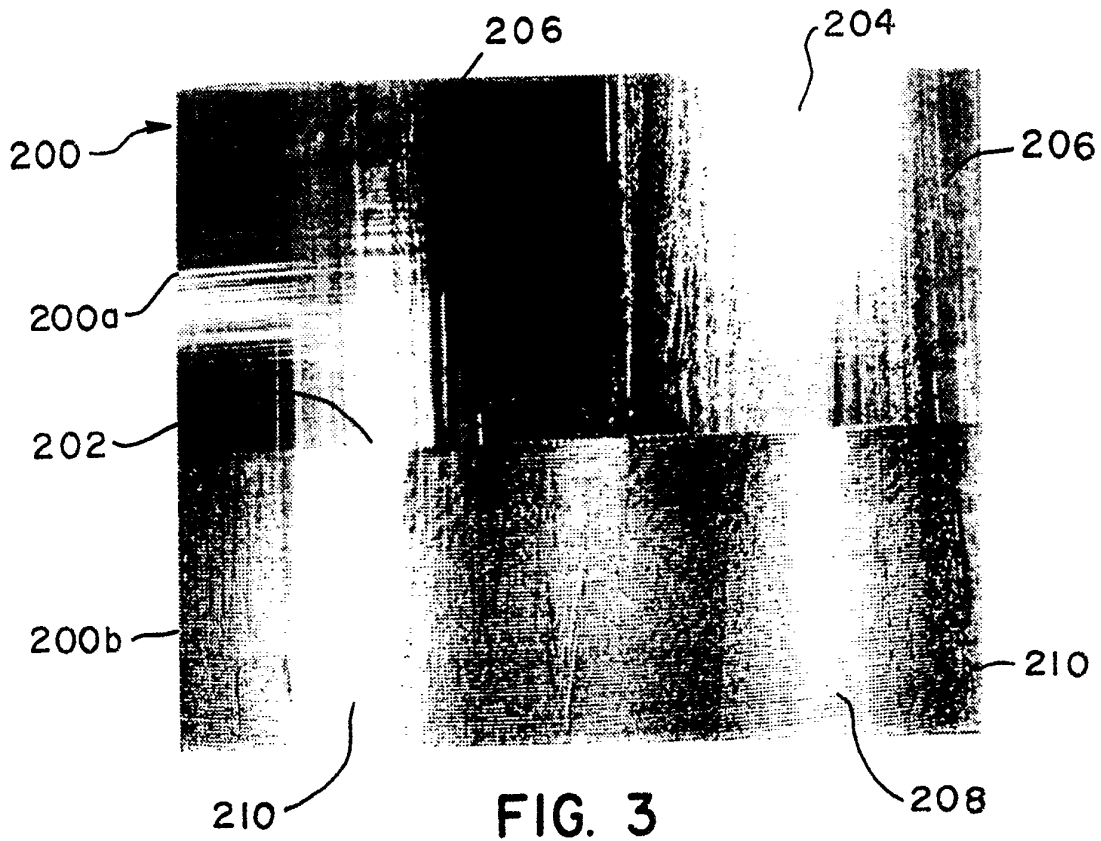
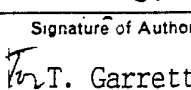


FIG. 3

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/05676

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT. CL. (5) BOLD 9/00 U.S. CL. 400/249		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
U.S.	156/608	156/6204 422/246
	156/617	156/Dig. 68 422/249
	156/618	156/Dig. 88 422/253
	156/620.1	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>9</sup>		
Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	US, A, 4,544,528 (STORMONT et al) 01 October 1985 (See entire document)	1-15
Y	US, A, 3,846,082 (LABELLE et al) 05 November 1974 (See entire document)	1-15
Y	US, A, 3,552,931 (DOHERTY et al) 05 January 1971 (See entire document)	1-15
A	"The Tubular Silicon Solar Cell-A New Concept For photovoltaic Power Generation"; Mlausky et al; MOBIL TYCO SOLAR ENERGY CORPORATION; p.p. 160-167	1-15
<p>* Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
19 December 1991		21 JAN 1992
International Searching Authority		Signature of Authorized Officer
ISA/US		 T. Garrett NGUYEN HOC-HO INTERNATIONAL DIVISION