View metadata, citation and similar papers at core.ac.uk

brought to you by CORE

provided by NASA Technical Reports Server

NOTICE

THIS DOCUMENT HAS BEEN REPRODUCED FROM MICROFICHE. ALTHOUGH IT IS RECOGNIZED THAT CERTAIN PORTIONS ARE ILLEGIBLE, IT IS BEING RELEASED IN THE INTEREST OF MAKING AVAILABLE AS MUCH INFORMATION AS POSSIBLE

NASA TECHNICAL MEMORANDUM NASA TM-75809

METHOD FOR HORIZONTALLY GROWING RIBBON CRYSTAL

Bossi Kudo

Translation of Japanese Patent Application No. 50-91099, Patent Publication No. Sho 52-15485 (July 28, 1975 application date), February 5, 1977, pp 437-441

(NASA-TM-75809) METHOD FOR HORIZONTALLY GROWING RIBBON CRYSTAL (National Aeronautics and Space Administration) 14 p HC A02/MF A01 CSCL 20B

N81-22951

Unclas G3/76 42205

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C. 20546 JUNE 1980

STANDARD TITLE PAGE

1. Report No. NASA TM-75809	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle METHOD FOR HORIZONTALLY GROWING RIBBON CRYSTAL		5. Report Date June 1980
		6. Performing Organization Code
7. Author(s) Bossi Kudo		8. Performing Organization Report No.
		10. Work Unit No.
9. Performing Organization Name and Address SCITRAN P. O. BOX 5456 SANTA BARBARA, CA 93108		11. Contract or Grant No. NASW-3199
		13. Type of Report and Period Covered Translation
12. Sponsoring Agency Name and Address		14. Sponsoring Agency Code

15. Supplementary Notes

Translation of Japanese Patent Application No. 91099/75, Application date July 28, 1975

Translation of Japanese Patent Application No. 50-91099, Patent Publication No. Sho 52-15485, (July 28, 1975 Application date), February 5, 1977, pp 437-441

16. Abstract

17. Key Words (Selected by Author(s))	18. Distribution Statement Unclassified - Unlimited

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
Unclassified	Unclassified	14	

NASA HQ

J-34

Patent Application July 28, 1975 *

To Honorable Hideo Saito, Chief, Patent Agency

1. Name of invention: Method of ribbon crystal growing by drawing horizontally.
2. Name of inventor: Bosshi Kudo, 60970 Higashifukai, Nagareyamashi, Chibaken
3. Patent applicant: Toyo Silicone Co., Ltd, 2-5, 1 Chome, Otemachi, Chiyodaku, Tokyo. Tsukasa Kobayashi, representative
4. Patent Attorney: Masahiro Takahash (and one other person) (5577), 1-4, 2 Chome, Marunouchi, Chiyodaku, Tokyo.

19 Patent agency of Japan

11 Patent publication No. Sho 52-15485

43 Date of patent application: February 5, 1977

21 Patent application number 50-91099

22 Application date: July 28, 1975

Request for investigation: Not submitted as yet (total 5 pages)

Intraagency processing number

7158 4A, 6521 57, 6452 42

---

52 Japanese classification

13 (7) D 522. 2, 99 (5) AO2, 10 A 41

51 Int. Cl.^{2}

BOIJ 17118

Detail

1. Name of invention

Method of ribbon crystal growing by drawing horizontally.

2. Extent of patent application.

---

* Translator's note: highly illegible foreign text.

METHOD FOR HORIZONTALLY GROWING RIBBON CRYSTAL

Bossi Kudo, Inventor

A high speed method of ribbon crystal formation is described. It is characterized by drawing out the formed ribbon crystal which is drawn out through a space formed by the front and back lines whose distance is more than 5.7 times that of the thickness of the grown ribbon crystal, which is the length of drawing out the upper part of the crystal body (hereinafter referred to as the growth domain) interface. It is drawn out between the molten body (hereinafter referred to as the back line) of the lower surface and the tip of the upper surface of the seed crystal, and growing crystal (hereinafter referred to as the front line). The method used causes the growth of ribbon type crystalline body at the tip of the seed crystal in order to grow the ribbon crystalline body with the desired width and thickness. The seed crystal (mentioned below) is drawn out the horizontal direction and centrifugally (hereinafter referred to as the direction of drawing out) by controlling the amount of cooling. This is done with the cooling mechanisms set up in order to cool the crystalline surface or the amount of heating by the heater mentioned below to control the temperature of the interface of the molten substance and its solid state crystals (hereinafter referred to as the growth interface) following the immersion of the ribbon formed seed crystal of the crystalline substance under consideration. The temperature is maintained about equal to the upper surface of the outlets of drawing out the molten substance, at least in certain portions of the crucible rim (hereinafter referred to as the drawing outlet) which is elevated so as to prevent dropping down of the molten raw material from the rim of the crucible as mentioned below. A horizontal drawing crystal formation furnace composed of chambers is used to form (iv) inactive atmosphere and support the items mentioned below, (iii) the mechanism to draw out the ribbon form crystal formed to the approximate direction of the horizontal line, ii) heating apparatus for the crucible, and i) the crucible that holds the raw material for the crystalline substance that is to be formed. These are the minimal components required for the horizontal drawing ribbon crystalline growing method.

3. Detailed explanation of the invention.

The recent trend of mass consumption of semiconductor devices in diodes, transistors, integrated circuits, etc., leads to the

immense potential demand for a solar battery that collects solar energy. Thus, crystalline substances which are basic materials for semiconductors (silicon), and insulators (sapphire), are in great demand for production. To achieve these ends, methods of producing wide, thin, and high quality ribbon type crystals are being sought. Various methods were devised to bring up the ribbon form crystal vertically. While these methods enabled a high rate of growth (300 illegible/minutes), various problems such as the crystalline defects, inevitable contamination, growth of only narrow width (less than several illegible) (the dendrite method), growth of relatively broad width (20-40 illegible) without appreciable degree of crystalline defects but slow rate of growth (less than several tens of illegible) (nondendrite & EFG methods), and requirements for delicate uplifting operation which is unstable (Webb method), precluded their adaptation in practice.

The horizontal drawing method invented by Bleil (USP, 3681033 or J. Crystal Growth, 1969) allows the molten crystalline substance under consideration in the crucible to rise around the crubicle rim. The ribbon seed crystal of that substance is immersed in the elevated portion around the rim. Thereafter, cooling the heat sink of the solid takes place while it is maintained in contact with the upper surface of the ribbon crystal. By drawing it out horizontally, ribbon crystal of the specified width and thickness is grown at the tip of the seed crystal. This method is characterized by the removal of heat coagulation generated at the growth interface with crystalline growth vertically from the upper surface of the seed and growth crystals. By doing this a thin and extensive cooling layer is readily formed on the surface of the molten substance. Thus it was possible to obtain relatively broad ribbon crystals with ice and Ge. However, since a solid was used in the heat sink noted above, some fluctuations in the cooling effect was caused by incomplete solid-solid contact occurred, which resulted in poor dimensional accuracy of the ribbon crystals grown, and the rate of speed of crystalline formation was slow. In order to improve on these points, Bleil pointed out that there are methods to remove the heat of coagulation by radiation, gases or liquids, but made

no mention of methods to increase the rate of crystalline formation.

The present invention solves the problems in the already known vertical and horizontal drawing methods of ribbon crystal formation. To achieve such objectives, as noted above, the horizontal drawing method was used, which is inherently suitable for thin and broad crystalline growth, The length of the growth domain was increased by controlling the amounts of heating and cooling by the heating and cooling apparatus which determine the temperature condition of the growth interface. This is made possible by making the distance between the front and back lines, that is, the tips of the upper surface of the seed and growing crystals (front line) and the drawn portion from the molten substance of the lower surface (back line), which forms the wedge-shaped crystalline body (growth domain), more than 5.7 times the thickness of the growing ribbon when it is drawn out. By doing so, a sufficient area for cooling to remove the large amount of heat of coagulation generated with the high rate of growth is produced and such a high rate of growth becomes possible.

A detailed description of methods employed in this invention is given below, using practical examples.

Figure 1 shows the major components in the crucible and state of drawing in the apparatus that produce ribbon crystals by the horizontal drawing method. The ribbon crystal, item 22, to be produced by this process, is drawn horizontally at the fluid level from a portion, item 23B (hereinafter referred to as the drawing out portion), of the free surface of the molten crystalline substance, item 1. The molten substance, item 1, is heated to the melting point by a resistance type or high frequency induction type heating apparatus, item 5, which receives controlled electrical current from a source not shown in the figure, and is held in a stable fashion horizontally by the crucible, item 3. The rim of the crucible is formed in such a manner that the entire rim, at least the drawing portion, is located slightly below the surface of the molten substance so that the process of drawing can be carried out without having the seed crystal or grown crystal

come in contact with the crucible rim. In order to raise the molten crystalline substance at the crucible rim and to support it in a stable fashion with surface tension, it is necessary to make the crucible from a material which does not react with or cannot be contaminated by the molten crystalline substance, and is not wettable. For example, in order to draw out semiconductor silicon ribbon crystal, the appropriate material for the crucible includes high purity quartz or high purity silicon, both of which are capable of supporting molten silicon in a stable manner raised to the height of about 1.0 illegible. When material that softens at high temperatures such as high purity quartz is used for the crucible, it is desirable to place it in another crucible, item 8, which is made of material such as high purity graphite, in order to maintain the system in a stable state. Also, in order to replenish the molten crystalline substance that is depleated as ribbon crystal is drawn out, a bar of raw material, item 2, such as a high purity silicon bar, for example, can be lowered from above by the holder, item 16, attached to the tip of the shaft, item 15. It can be heated by the resistance or high frequency induction type heating apparatus, item 7, which receives electricity from the electrical control apparatus not shown in the figure, through the crucible made of material such as quartz, item 4, and a graphite crucible, item 9, to melt the lower portion of the bar. This controls the fluid level of the molten substance at the drawing region at a certain constant height. Needless to say, the same process could be used for the initial formation of the molten substance, item 1. The temperature of the melting portion is higher than that of the drawing portion because of the necessary heat of melting. Solids such as SiO are formed, when semiconductor silicon is treated, on surfaces of the inner wall of the quartz crucible, item 4, raw material bar, item 2, supporting equipment, item 16, shaft, item 15, etc. These solid pieces drop on the molten substance, reach the drawing portion, causing the growth of abnormal crystals. The lower portion of the quartz crucible, item 4, is partially immersed in the molten substance, item 1, to separate floating solids, item 26. The vibrations of the liquid surface due to melting are prevented from being transmitted to the drawing portion by insulation of the quartz crucible, item 4.

Furthermore, the surface of the molten substance which has been replenished by the method mentioned above and is controlled to maintain a constant height. It is first controlled to the appropriate temperature at around the location 25 by the heating apparatus (top heater), item 17. Prior to the growing the ribbon crystal, item 22, it arrives in a certain territory, that is the forefront of the front line, item 24F, of the growth domain. Then it is cooled by cold inert gas such as Ar, blown downward from a nozzle such as a quartz nozzle, with a controlled rate of flow, which constitutes the tip of the gas cooler, item 19. This results in the formation of a supercooled surface portion, to the temperature slightly below that of solidification of the crystalline material (1420°C in case of silicone). The ribbon crystal forms in the growth domain between F-B. The supercooled surface layer formed outside the growth interface absorbs a large amount of heat of coagulation generated during a rapid rate of growth, on the molten substance side as well. This offers a powerful means for the realization of a high rate of growth. Also, in order to remove the large quantity of heat of coagulation generated at the growth interface effectively, the upper surfaces of seed crystal and ribbon crystal within the growth domain are cooled by the cooling apparatus, item 19, as well. Through this process, the crystalline surface immediately above the growth interface that is separtated only the thickness of the thin grown ribbon crystal forms a cooling surface with a large area. This offers another powerful means for the realization of a high growth rate. The present invention utilizes this action in the most effective manner. Thus, by adjusting the cooling of the surface of molten substance at the drawing portion by the cooling apparatus, item 19, and heating from the lower portion of the molten substance of the drawing portion where the depth is relatively small using the heater, item 5, a cooling layer is created with a large (isothermal) area of coagulation with a uniform depth in the direction at right angles to the direction of drawing. It has a gradually increasing depth toward the back line B, with approximately D at the front line F in the direction of drawing. It is situated on the surface of the molten substance. Here, in case of

a ribbon form seed crystal, semiconductor silicon, that has the same structure as the crystal that is being drawn, a thin monocrystalline plate with the main surface of (1 1 1) and the direction of drawing is <2 1 1> can be immersed for adaptation. This can be followed by drawing the desired ribbon crystal, by recrystallization, using the growth domain at the tip of the seed crystal or growing the ribbon crystal (continuously from seed crystal or growing ribbon crystal). The use of a drawing out apparatus is used (For example, maintaining a constant level by guide rollers made of graphite, such as items 20 and 21, and furthermore, while not included in the illustration, using a motor-powered drive roller covered with material such as silicon rubber, to draw out ribbon crystal that is sufficiently cooled in the horizontal direction). The present invention pertains to the method that allows a high rate of growth in the method of horizontal ribbon crystal formation as described above. As noted above, by adjusting heating of the lower portion of the molten substance, item 1, with the heater, item 5, and cooling from the upper portion of the growth domain with the cooler, item 19, the morphology of the growth domain that is being drawn out is such that its perpendicular cross section in the direction perpendicular to the drawing direction is maintained at a constant thickness. The perpendicular cross section in the direction parallel to the drawing out direction is wedge-shaped, as shown in figure 2, with gradually increasing thickness from the front line, F, toward the back line B. However, as shown in figure 1, by moving the location of the cooling apparatus, item 19, in the direction opposite to the drawing out direction , so as to increase the distance L between the points F and B and make it greater than 5.7 times the thickness of the growing ribbon, it is possible to attain a ribbon crystal growth which conventional methods cannot attain.

When a ribbon crystal with thickness, t, and width, w, is being grown at the drawing velocity, rd, the heat of coagulation Qf generated on the entire growth interface between the points F and B can be expressed as:

[illegible] (1)

(here, Sc: specific gravity of the crystalline substance, 9mp: heat of coagulation of the crystalline substance per unit weight).

When the vertical angle θ of the wedge is sufficiently small, the area of the growth interface is equal to the product of the length of the growth domain L and the width of the crystal w, so that the heat of coagulation per unit area of the growth interface, qf, becomes:

$$q_f = vt \cdot - \cdot S_c \cdot q_{mp} = v \cdot \tan\theta \cdot S_c \cdot q_{mp} \quad (\tan\theta = t/L). \tag{2}$$

Accordingly, in order for the crystalline growth to continue, this qf has to be completely emiminated both by the supercooled layer of the molten substance that surrounds the growth interface and the crystalline body of the growth domain. Since there is a limit, q, to the amount of heat removed from a unit area of growth domain by a cooling apparatus of given performance capacity, in order to cause faster crystalline growth, it is necessary to decrease the vertical angle, θ of the wedge, in other words, to increase the length, L, of the growth domain in comparison with the thickness, t. The qL mentioned above varies with capacity of the cooling apparatus used. The values of θ or t/L will have to be determined empirically. However, in experimental results by the inventor and others, in which ribbon crystal of semiconductor silicon with thickness 1 illegible and width 40 illegible was drawn out, a high quality monocrystal was obtained at a high rate of 300 illegible/minute, heretofore unheard of with conventional methods, using E_2 gas cooling apparatus with $\theta = 1^{\circ}\ 10'$ or 1=50 illegible, confirming the practicality and efficiency of the present invention. In order to effectively use the horizontal drawing method over the conventional vertical drawing method, it was necessary to have L above 5.7t, that is θ at less than 10°.

In the foregoing explanation, a description was given in which the direction of drawing is horizontal. But various combinations, some 15 as shown in figure 3, of major drawing methods are possible, where the level of the front line F is higher than, equal to, or lower than the surface of the molten substance, the

upper and lower surfaces of the growth domain are above over F°, the lower surface is on the same level as F but the upper surface rises and the lower surface drops, the upper surface is on the same level as F and both the upper and lower surfaces descend below F, etc. In any of these combinations, it goes without saying that as long as the direction of drawing is only slightly slanted at small angles to the horizontal direction, and as long as the direction of drawing is horizontal or close to it, the methods of the present invention are applicable.

Furthermore, although the foregoing explanation had to do with situations in which the seed crystal and ribbon crystal are monocrystals, it is obvious that the present invention applies to polycrystals as well.

4. Simple explanation of illustrations.

Figures 1-3 show the apparatus used for the present invention. Figure 1 shows the cross section of the main structure of apparatus producting ribbon crystal by the horizontal drawing method and the drawing state of the ribbon. Figure 2 is the cross section in the direction perpendicular to the ribbon crystal drawing direction. It the wedge shaped crystalline formation domain with gradually increasing thickness from the front line F toward the back line B. Figure 3 shows cross sections of various examples when the drawing direction is changed with slight angles to the horizontal line.

In each figure:

1: Molten crystalline substance

2: Bar of raw material

3,4: Quartz crucible (the portion that holds the molten substance is designated as 3, and the portion that surrounds the bar of raw material, 2, is designated as 4).

5, 6, 7, 17: heating apparatus

8, 9: graphite crucible (the portion that holds the molten substance is designated as 8, and the portion that surrounds the bar of raw material 2, is designated as 9).

10, 11, 12, 13, 18: heat preserving apparatus

14: support shaft for the apparatus
15: support shaft for the raw material bar, 2.
16: support structure
19: gas cooler
20, 21: guiding roller
22: ribbon crystal
23B: back line
24F: front line
L: Distance between F and B
25: optional position
26: floating solids
t: thickness of ribbon
θ: vertical angle of the wedge

Applicant: Toyo Silicone Co. Ltd.
Patent attorney: Masahiro Takahashi
and 1 other person

Fig. 1. a) molten portion b) drawn portion
c) gas

5. List of attached papers
   (1) details, 1 copy
   (2) Illustrations, 1 copy
   (3) Letter of attorney 1 copy
   (4) Duplicate application 1 copy
6. Attorney other than noted above
   Eiichi Sakamoto (6667)
   Section 785, Marunouchi Building,
   1-4, 2 chome, Marunoushi
   Chiyodaku, Tokyo.

Fig. 1

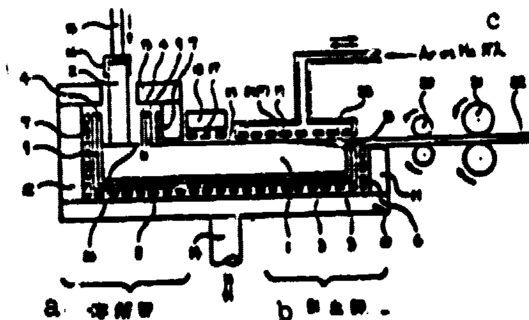

Fig. 2

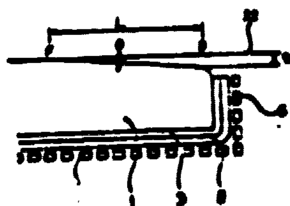

Fig. 3