Aug. 1, 1972 C. E. BLEIL 3,681,033

HORIZONTAL GROWTH OF CRYSTAL RIBBONS

Filed Jan. 31, 1969

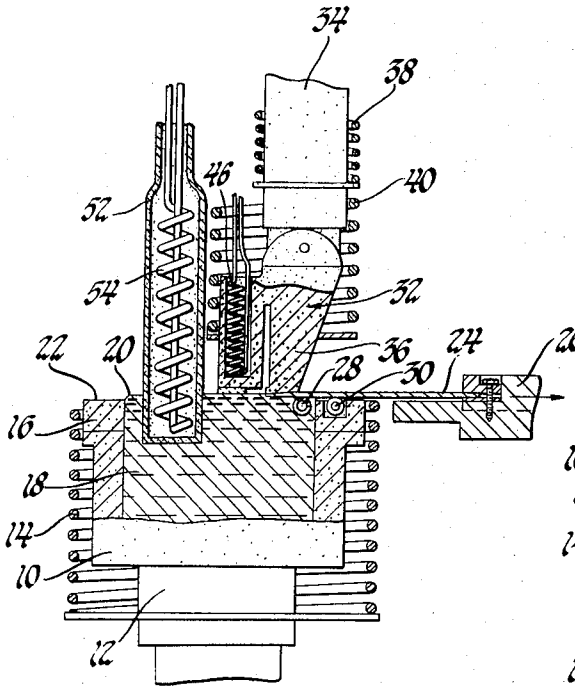


Fig. 1

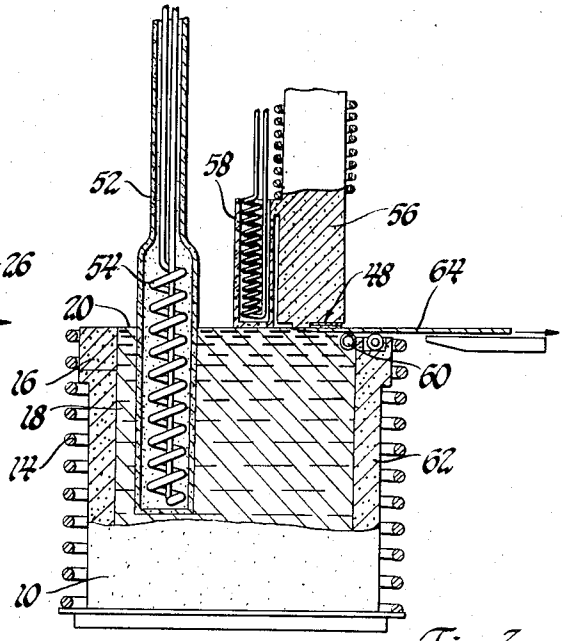


Fig. 3

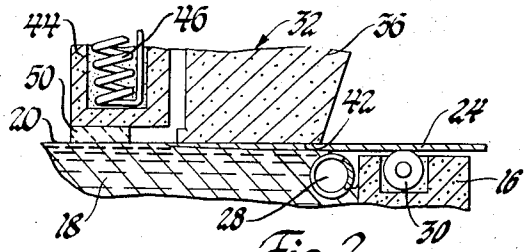


Fig. 2

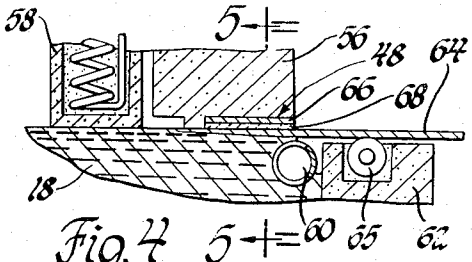


Fig. 4

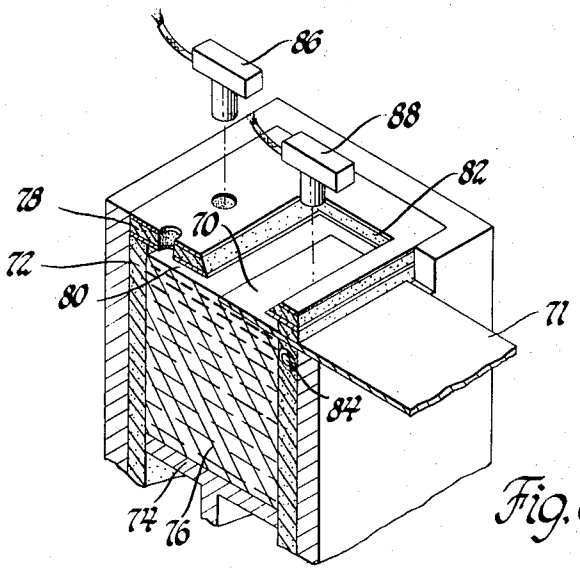


Fig. 6

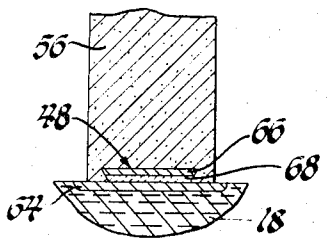


Fig. 5

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HORIZONTAL GROWTH OF CRYSTAL RIBBONS

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Filed Jan. 31, 1969, Ser. No. 795,561
The portion of the term of the patent subsequent to Sept. 21, 1988, has been disclaimed
Int. Cl. B01j 17/18
U.S. Cl. 23—273 SP 3 Claims

ABSTRACT OF THE DISCLOSURE

A method and apparatus is described for horizontally pulling crystal ribbons from a melt parallel to the melt surface. The heat of crystallization is selectively removed from one end of a seed crystal by a heat absorbing means perpendicular to the melt surface. Means are provided to appropriately suppress net loss of the heat of fusion from the balance of the seed in contact with the melt to control the thickness of the resultant ribbon.

BACKGROUND OF THE INVENTION

Thin wafers of monocrystalline semiconductive materials are generally produced from monocrystalline boules grown by the Czochralski technique. The preparation of the thin wafers from the large crystal boule, as is well known, is a costly and time-consuming technique, inherently wasting much of the boule. Consequently, much effort has been directed toward growing thin monocrystalline ribbons, that need only be scribed and broken to be used. In addition, where larger area wafers are desired, more slender boules have been grown, so that the boules need only be sliced to be used. However, most devices require small area wafers, and thin ribbon growth is much more alluring. Thin ribbons have been grown through elongate openings in a melt cover. In this latter technique the crystal is pulled perpendicular to the surface of the melt through a melt cover slot, so that the transverse cross section of the resultant ribbon conforms generally to the shape of the slot. However, satisfactory larger ribbon widths are extremely difficult to produce by means of this latter technique, and processing of the smaller ribbon widths is not commercially advantageous. Also, it has been proposed to horizontally produce flat ribbons by zone melting techniques. However, such techniques have not been wholly satisfactory for producing thin ribbons of high purity.

SUMMARY OF THE INVENTION

It is, therefore, a principal object of this invention to provide a means for pulling relatively wide, high purity, thin crystalline ribbons directly from the surface of a melt. In particular, it is an object of this invention to provide a method and apparatus for pulling a crystalline ribbon horizontally from a melt. These and other objects of the invention are attained by placing a thin flat seed in contact with the surface of a melt, and withdrawing the heat of fusion generally perpendicularly from one end of the seed while maintaining the crystal-melt freezing isotherm coextensive with the desired ribbon thickness. This isotherm is maintained by suppressing the net loss of the heat of fusion from the balance of the seed. The seed is simultaneously pulled parallel to the surface of the melt at a rate commensurate with the rate at which the melt progressively solidifies on the end where heat is being withdrawn. In a preferred embodiment a heat sink is placed in contact with the end of the seed where growth is desired, and supplementary heaters and/or heat reflectors are used to suppress net loss of the heat of fusion from the balance of the seed. In one embodiment for growing

semiconductor ribbons, the seed is wider than the contact surface on the heat sink, and the rate of pull is controlled so that the heat sink contacts only the growing seed, not the melt.

BRIEF DESCRIPTION OF THE DRAWING

Other objects, features and advantages of the invention will become more apparent from the following description of preferred examples thereof and from the drawing, in which:

FIG. 1 shows an elevational view in partial section of the melt area of a Czochralski-type crystal growing apparatus modified with a heat sink for horizontal crystal growing in accordance with the invention;

FIG. 2 shows an enlarged fragmentary view of the melt-seed-heat sink contact region of the apparatus shown in FIG. 1;

FIG. 3 shows an elevational view in partial section of a modification of the apparatus shown in FIG. 1, in which the heat sink includes a heat reflector to aid in controlling thickness of the crystalline ribbon grown;

FIG. 4 shows an enlarged fragmentary view of the melt-seed-heat sink contact region of the apparatus shown in FIG. 3;

FIG. 5 shows a transverse sectional view along the line 5—5 of FIG. 4; and

FIG. 6 shows an isometric view in partial section of another apparatus for horizontal crystal growing contemplated by the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As previously indicated, the principal feature of this invention lies in the selective removal of heat perpendicular to the surface of the melt at one end of a crystal seed on the surface of the melt, and the suppression of the net loss of the heat of fusion from the balance of the crystal seed. A heat sink can be used to selectively remove the heat of crystallization from the one end of the seed as shown in connection with FIGS. 1 through 5. On the other hand, the heat can be removed by simply allowing it to radiate to the ambient, as shown in FIG. 6. The end of the seed where the heat is lost becomes the growing end of the resultant ribbon. Growth is suppressed in the balance of the ribbon, so that its thickness is controlled. If thickness is not controlled at all, the ribbon may become so thick that it cannot even be pulled over the lip of the melt crucible. Growth can be suppressed by suppressing net loss of the heat of fusion. It can be suppressed with a special heater to replace any heat of fusion loss or with a heat reflector to suppress any actual loss of the heat of fusion, or both. Hence, by net heat loss I mean that if there is any actual loss of the heat of fusion it is replaced by a heat source other than the melt itself. Hence, this heater and/or the heat reflectors establish a freezing isotherm for the balance of the ribbon contacting the melt that is coextensive with the desired ribbon thickness. When the growing seed is pulled horizontally across the surface of the melt, it moves through the area where further crystal growth is controlled as desired.

The surface of the seed facing the heat absorber should be coplanar with the surface of the melt, at least adjacent the growing tip of the seed. By growing tip I refer to the transverse edge of the seed on its growing end where growth opposite the direction of pull occurs. The growing tip can be made coplanar with its adjacent melt surface, by making the entire upper surface of the seed coplanar with the free surface of the melt. It can also be done by using a separate melt contact element, having a surface that is wetted by the melt, to lift the melt by surface tension forces to the desired level adjacent the seed

growing tip. I prefer to use both principles to insure seed-melt coplanarity.

Moreover, the new growth on the seed may or may not adhere to the heat sink removing means. The crystal can be prevented from adhering to the contacting surface of the heat sink if there is no strong reaction between their contacting surfaces near the crystal melting point. For example, ice forming on a Teflon coated sink does not significantly adhere to it. If crystal-heat sink adherence is a problem, nucleation of the crystal must be induced away from the heat sink. This can readily be accomplished by starting with a seed that is wider (and, of course, much longer) than the seed contact area of the heat sink, generally centering the heat sink between the sides of the seed, spacing the heat sink back somewhat from the tip of the seed where growth is desired, and pulling the seed at an appropriate rate or adjusting the rate of nucleation to substantially maintain this spacing during crystal growth.

Of course, the usual precautions pertaining to the choice of crucible materials, ambient atmosphere, vibration-free environment, and other routine growth conditions should be observed for this invention as one would in the usual Czochralski crystal growing technique.

More detailed aspects of the invention can best be described by reference to the drawing. FIGS. 1 and 2 show the melt crucible area of a germanium crystal growing apparatus made in accordance with the invention. To better focus attention on the improvements this invention presents, the ancillary features normally incident to a Czochralski-type crystal growing apparatus, such as a housing and support means for producing a protective environment, heater power supplies, pulling apparatus and the like, are not shown. However, for example, the apparatus would involve a Pyrex furnace chamber, heating power supplies, means for producing and maintaining in it an atmosphere of 2 parts argon and 1 part hydrogen, etc.

In the crucible area of the grower, a rectangular graphite crucible **10** rests on a crucible support **12** within an encircling radio frequency type heater **14** for heating the crucible to a temperature of about 960° C. The crucible **10** has an inner dimension of 2½ x 1⅜ x 1¼ inches and has a ½ inch high graphite collar **16**. It is slightly overfilled with a 540 gram melt **18** of germanium, so that the free melt surface **20** is held about 0.06 inch above the lip **22** on crucible collar **16**.

One end of a monocrystalline seed **24**, ½ inch wide and 0.03 inch in thickness, contacts the surface **20** of the melt. The major faces of the seed are parallel and in the (111) plane. The other end of the seed **24** is connected to a puller **26** for pulling it in the <211> direction. The seed is, therefore, pulled horizontally so that it, in effect moves parallel over the surface of the melt. A special heater **28** is recessed in the surface of the melt under the seed adjacent the crucible wall over which the seed is pulled. It lies parallel that wall and transverse to the ribbon being formed to supply ribbon heat lost by radiation. It is spaced only about 0.010 inch below the ribbon and is adjusted to maintain the freezing isotherm in the system coextensive with the desired ribbon thickness. A spring loaded roller support **30** in the crucible collar **16** supports the ribbon as it is pulled over the lip **22** of the crucible.

The growing tip of the seed **24**, opposite that end which is attached to the puller **26** contacts the surface **20** of the melt under a heat sink **32**. The heat sink has a graphite cylindrical supporting shaft **34** one inch in diameter and a graphite cooling shoe **36**. The supporting shaft **34** is cooled by cooling coils **38**. The cooling shoe **36** is heated by an induction heater **40** to raise it to the temperature desired to support the particular rate of crystal growth. The lower surface **42** of the shoe **36** is rectangular, being about one-half inch wide and one inch long. It is somewhat narrower than the seed and generally centered between the seed edges, as previously described. Also as previously described, it is spaced inward of the growing tip of the seed so that it does not contact the melt directly.

The shoe portion **36** of the heat sink also serves as a support for appendage **44**, which contains an auxiliary heater **46**. The heater **46** in appendage **44** aids in more precisely controlling melt temperature at the growing tip of the seed, the principal growth interface. The bottom end of the appendage has a projection **50** thereon of a substance that its wetted especially well by the melt, such as quartz. The bottom surface of projection **50** is coplanar with the seed contact area of the heat sink and is a one-half inch square area, and spaced 0.25 inch from the contact surface of the heat sink. Being wetted by the melt, projection **50** serves to maintain the melt surface adjacent the growing tip of the seed coplanar with the top surface of the seed, even if that seed surface should vary somewhat from the level of the free surface of the melt. Since the seed floats on the surface of the melt, it is maintained coplanar therewith by the downward force of the heat sink. By mounting appendage **44** on the heat sink, the melt surface adjacent the growing tip of the seed can be maintained coplanar with the seed top surface even when the free melt surface is not.

A graphite bulb **52** having heater **54** is used as a melt level controller to make the process more continuous. The bulb **52** is progressively immersed more deeply into the melt as the crystal ribbon is formed to maintain the free surface of the melt substantially constant. It can be interconnected with the pulling apparatus (not shown) to maintain melt level automatically.

FIGS. 3 through 5 show a modification of the apparatus illustrated in connection with FIGS. 1 and 2. The modification involves the construction of the heat sink used to selectively remove heat from the seed and the nature of the special heating used to maintain the desired freezing isotherm. The heat sink **56** in FIGS. 3 through 5 is of a unitary construction and is wholly of graphite. Also, it contains a heat reflector section **48** to better control ribbon thickness and cross-sectional geometry.

Since the heat sink **56** in FIGS. 3–5 is of graphite, no special contact projection need be provided for the growth interface control appendage **58** attached to it. While a quartz surface might be wetted better, the graphite surface is adequate. However, since germanium will adhere to graphite when it solidifies, the growth interface on the end of ribbon must be maintained between the appendage **58** and the main body portion of the heat sink, just as described in connection with FIGS. 1 and 2.

As in FIG. 1, a special heater **60** is used in the melt along the crucible wall **62** underneath the ribbon **64** so that the ribbon passes closely over it as it breaks contact with the melt. However, complementing heater **60** in controlling ribbon thickness is the heated roller **65** in the crucible wall **62**. If desired, the heated roller **65** can be used as the principal source of heat to control the adjacent melt-crystal freezing isotherm. Complementing both the special heater **60** and the heated roller **65** is the heat reflector **48** in the adjacent end of the heat sink **56**. The heat reflector can be of a laminate of a nickel sheet **66** and an outer quartz sheet **68**. The heat shield suppresses radiation of heat from the non-growing end of the seed in contact with the melt. It not only suppresses thickening of the ribbon but also makes the bottom surface of the ribbon flatter. The heat reflector need not be made as a part of the heat sink, but the heat sink provides a convenient support. Using both the auxiliary heaters **60** and **65** under the ribbon and a heat shield over the ribbon, thickness can be more accurately controlled.

FIG. 6 illustrates a still further modification of the invention. FIG. 6 shows how heat can be selectively removed from one end **70** of the growing crystal **71** and heat loss suppressed in the balance of the crystal contacting the melt without even using a discrete heat sink element. The melt is contained in a graphite crucible **72** having a piston **74** for its bottom wall. Upward movement

of the piston controls the level of the melt **76** within the crucible. Means for heating the crucible to a suitable temperature and for providing the usual crystal growing environment are not shown. The crucible is provided with a heat reflective cover **78** spaced from the upper surface of the melt to reflect back heat irradiated by the surface **80** of the melt. The cover can be of graphite having a heat reflective coating on its surface. A rectangular aperture **82** is provided in the surface of the cover of a width commensurate with the crystalline ribbon width desired. It is of a length (with respect to the axis of pull) sufficient to obtain the desired ribbon thickness. Heat is selectively removed from the growing end **70** of the ribbon **71** by permitting radiant heat loss from the growing end of the ribbon to the surrounding environment. Actual heat loss from the balance of the seed in contact with the melt is suppressed by means of the heat reflective metal cover. Net heat loss in the balance can be further suppressed if desired by means of a special heater **84** in the crucible wall over which the crystalline ribbon is pulled. Hence, analogous to the apparatus of FIGS. 3–5 a special heater and a heat shield are used. It may even be desired to supplement this by means of a special heater (not shown) within the melt itself adjacent the crucible wall over which the crystal ribbon is pulled, as in the apparatus shown in connection with FIGS. 3–5. The process can be conducted continuously by means of automatic sensors **86** and **88** to determine melt level and temperature, respectively.

It is to be appreciated that although this invention has been described in connection with certain specific examples thereof, no limitation is intended thereby except as defined in the appended claims.

I claim:

1. An apparatus for horizontally growing a crystalline ribbon-like body which comprises means for containing a melt for crystal growing, said melt having an upper surface, means for holding a crystalline seed in contact with said melt surface, said seed having an upper surface, means contacting said seed surface for removing heat affecting crystallizing growth from one end of said seed, a heater below said melt surface at the pull end of said heat removing means for controlling thickness of said seed, and means for horizontally pulling said seed over said heater away from said heat removing means at a rate commensurate with the rate of growth on said seed one end to thereby produce a flat crystalline ribbon of predetermined thickness.

2. The apparatus as described in claim **1** wherein the heat removing means contacting said one end of said seed includes means for maintaining said upper surface of said melt adjacent said one end of said seed coplanar with said upper surface of said seed.

3. An apparatus for horizontally growing a crystalline ribbon-like body which comprises means for containing a melt for crystal growing, said melt having an upper surface, means for holding a crystalline seed in contact with said melt surface, said seed having an upper surface, means contacting said seed surface for removing heat affecting crystallizing growth from one end of said seed, a heater below said melt surface at the pull end of said heat removing means for controlling thickness of said seed, means for horizontally pulling said seed over said heater away from said heat removing means at a rate commensurate with the rate of growth on said seed one end to thereby produce a flat crystalline ribbon of predetermined thickness, means for maintaining said upper surface of said melt at a generally constant level as melt volume decreases during crystallizing growth onto said seed, and means for maintaining said melt upper surface immediately adjacent the tip of said seed one end precisely coplanar with said seed upper surface.

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U.S. Cl. X.R.

23—301 SP

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,681,033 Dated August 1, 1972

Inventor(s) Carl E. Bleil

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, after the title, "Carl E. Blyeil" should read -- Carl E. Bleil --.

Signed and sealed this 23rd day of January 1973.

(SEAL)
Attest;

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents