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METHOD AND APPARATUS FOR PRODUCING CRYSTALLINE SEMICONDUCTOR RIBBON

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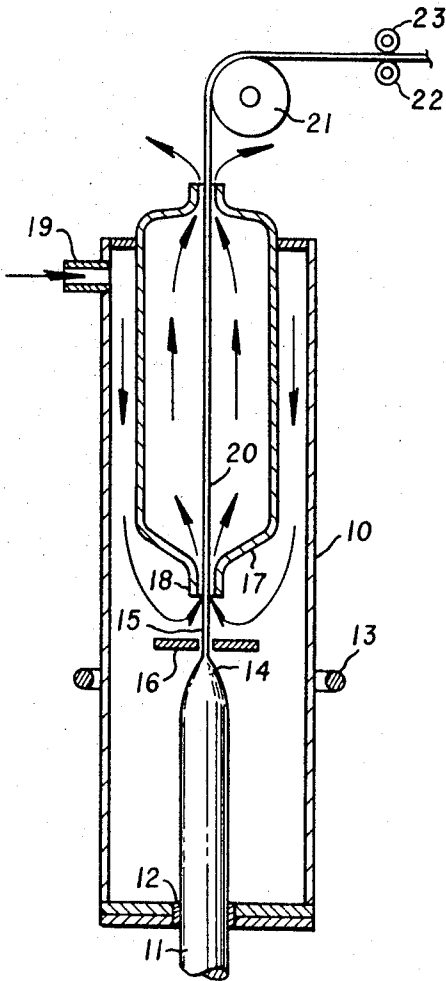


Fig. 1

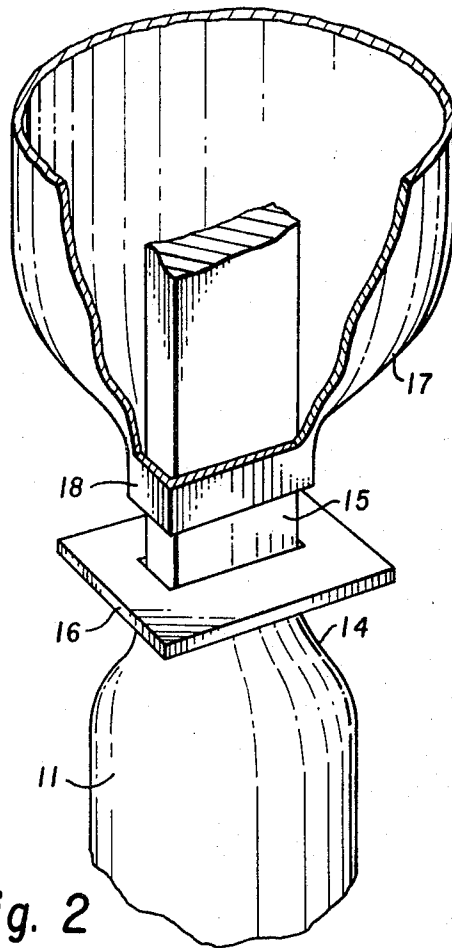


Fig. 2

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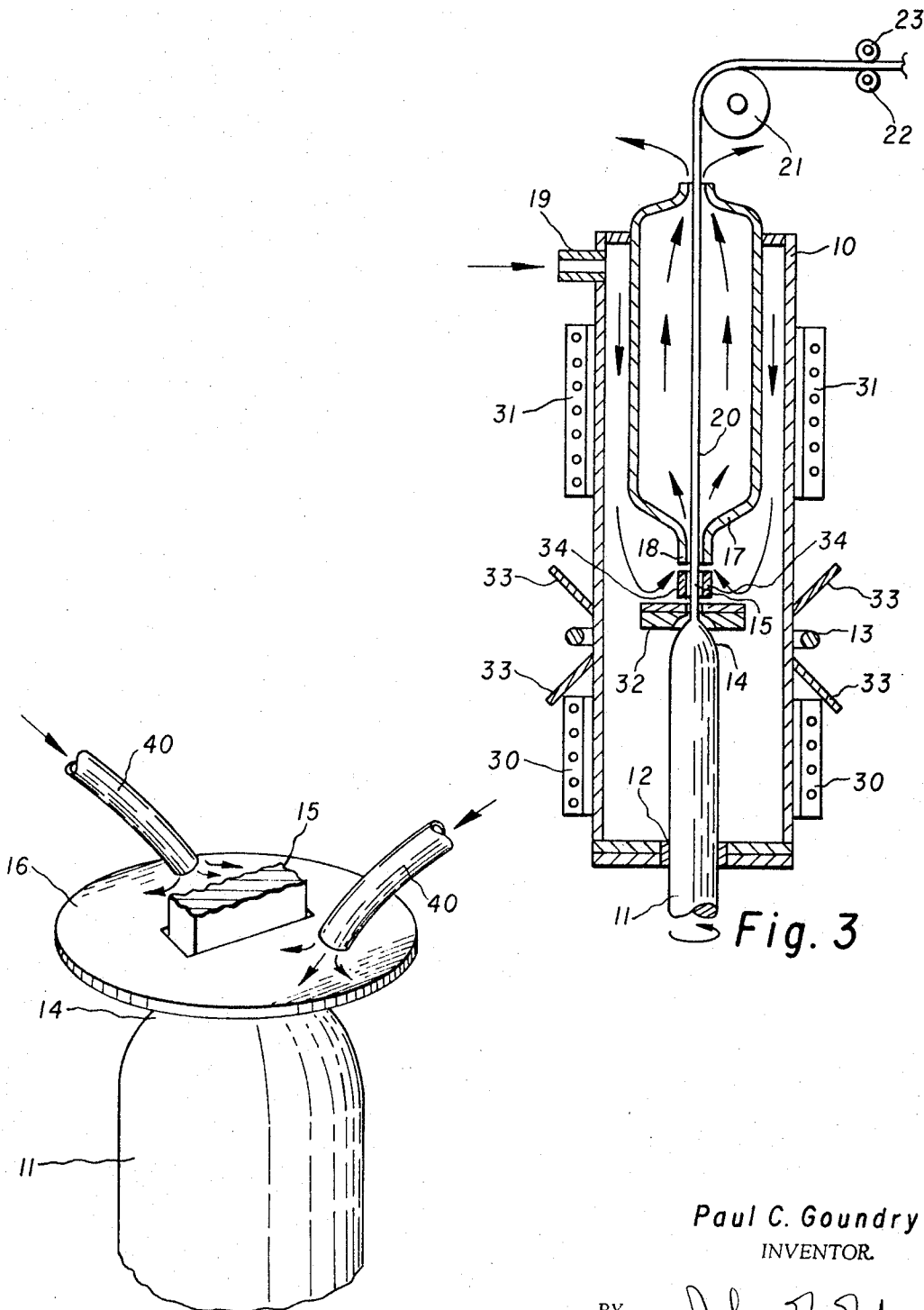


Fig. 4

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METHOD AND APPARATUS FOR PRODUCING CRYSTALLINE SEMICONDUCTOR RIBBON

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Int. Cl. B29c 25/00

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13 Claims

ABSTRACT OF THE DISCLOSURE

This specification discloses a method of continuously forming a monocrystalline ribbon of semiconductor material, characterized by the steps of:

- (a) drawing liquid semiconductor material through an aperture in a shaping guide, the aperture corresponding to the cross-sectional dimensions of the monocrystalline ribbon to be produced and shaping the ribbon by physical contact;
- (b) maintaining the temperature of the liquid semiconductor material above the freezing point of the semiconductor material while within the shaping guide but freezing the semiconductor ribbon in an isothermal zone immediately thereabove, the freezing taking place before surface tension of the semiconductor material can distort the shape induced by the shaping guide and unconstrained by physical barriers so as to effect a substantially planar freezing zone parallel with the shaping guide whereby monocrystalline ribbon is effected; and
- (c) continuously removing, during formation of the ribbon, the ribbon of semiconductor material which has been frozen.

One method of effecting the desired freezing is by:

- (a) drawing the liquid semiconductor material through a second aperture having substantially the cross section dimensions of the ribbon to be produced; and
- (b) passing the cooling gas through the second aperture whereby the gas flows between the sides of the aperture and the semiconductor material, the gas serving to automatically control the size of the monocrystalline ribbon. Apparatus enabling carrying out the method is also disclosed and includes specific refractory metals to form the shaping guides so they are not wet by the molten semiconductor material, as well as heat reflectors and other temperature regulating means to effect the desired thermal gradients.

This is a continuation-in-part of application Ser. No. 418,043, now abandoned filed Dec. 14, 1964, entitled "Method of Producing Crystalline Semiconductor Ribbon." The invention relates to methods of and apparatus for producing crystalline semiconductor material, and more particularly to continuous processes for producing monocrystalline semiconductor material in ribbon form.

As used herein the term "ribbon" means a flat semiconductor crystal relatively long in a first axis, wide in a second axis (width being less than length), and extremely small in a third axis (the thickness being much less than the width or length).

The increasing demand for greater reliability of semiconductor devices and continued pressures for reduced costs have produced extensive mechanization of semiconductor manufacturing processes. Such mechanization is based on the effective utilization of slices of single crystal material prepared from grown crystals and has provided certain improvements in quality and cost reduc-

tion. However, these techniques have been limited to batch-handling of large numbers of slices, thus no continuous process of producing monocrystalline semiconductor material has heretofore been evolved. Furthermore, operations such as sawing, lapping, polishing and etching of the crystal slices to prepare them for fabrication into semiconductor devices result in large wastes of the original monocrystalline semiconductor crystal. Only approximately 35% of the starting material is ultimately used in devices.

The prior art has attempted to solve the above problem by producing semiconductor material in the form of a crystalline web grown between dendrites. However, this process has many inherent limitations. Producing a silicon ribbon between two dendrites requires that the dendrites be grown from a super-cooled melt because dendritic growth actually occurs below the liquid level in super-cooled regions. The dendritic growth temperature is about 5° C. to about 15° C. below the normal melting point. When this super-cooled region is established it must be held at essentially a fixed temperature by a control system which operates with a precision of about $\pm 0.01^\circ$ C. Critical thermal gradients in the crucible and cover system must be maintained to support the super-cooled region necessary for dendritic growth; a complex and difficult control requirement for a manufacturing process.

The requirements for seed crystals which will initiate dendritic ribbon growth are quite critical. Suitable seeds must have twin planes parallel to the growth direction and the number and spacing of these twin planes are critical. Furthermore, the twin planes in the seed are propagated throughout the growing web and are present in the finished material.

The presence of dendrites along the edges of the semiconductor ribbon poses problems in device manufacturing. The use of this material for epitaxial depositions or diffusions generally requires the absence of the dendrites. Thus the dendrites must be removed by scribing and breaking, etching or electron beam cutting. However, these techniques contaminate or damage the web material and add processing costs to the finished ribbon.

The dendritic ribbon growth requirement of a super-cooled melt makes the development of a continuous process impractical. The addition of new charge material to the melt would disturb the critical thermal gradients and terminate growth, thus limiting the total length of ribbon which can be grown to the batch size.

It is therefore an object of the present invention to provide a continuous process for producing monocrystalline semiconductor material. Another object is to provide a method of and apparatus for producing monocrystalline material in thin ribbon form which may be directly used for fabricating semiconductor devices without further processing. A further object is to provide an apparatus for shaping liquid semiconductor material into a thin ribbon and controlling the temperature of the ribbon to from a monocrystalline semiconductor ribbon.

In accordance with a specific embodiment of this invention, crystalline bar stock or rod of purified semiconductor material is continuously fed into a controlled atmosphere chamber. Within the chamber the end of the crystalline bar stock is melted to form a small region of molten semiconductor material which is supported on the end of the bar by its own surface tension. A crystalline ribbon is drawn from the melt by dipping a monocrystalline seed crystal of the desired shape and orientation into the molten semiconductor. The seed is then withdrawn, drawing with it a ribbon of molten semiconductor. The molten ribbon is drawn through a shaping guide which shapes the molten ribbon into the desired shape and size. The guide provides an isothermal rectangular plane which

controls the temperature of the liquid semiconductor passing therethrough. The molten ribbon is then drawn through a second aperture and into a second chamber. The orifice through which the molten ribbon enters the second chamber is of substantially the cross-sectional dimensions of the desired crystalline ribbon. A cooling gas is forced into the second chamber between the walls of the orifice and the liquid semiconductor ribbon to provide cooling and crystallization of the semiconductor. The cooling gas passing through the orifice provides an automatic control of the shape and size of the crystalline ribbon by providing a second isothermal rectangle which is at the freezing point of the semiconductor.

A particular advantage of this invention is the formation of a ribbon by the shaping guides rather than web growth between dendrites. The product is all monocrystalline semiconductor ribbon without twin planes and without dendrites. Another advantage is the growth of a monocrystalline semiconductor material from a melt supported on the end of a semiconductor bar, thus avoiding contamination of the melt with impurities from a crucible and providing a continuous process.

Other objects, features and advantages will become more readily understood from the following detailed description taken in conjunction with the appended claims and attached drawing, in which:

FIGURE 1 is a diagrammatic representation partially in cross-section of apparatus suitable for practicing the invention,

FIGURE 2 is a cutaway view of the second chamber and shaping guide,

FIGURE 3 is a diagrammatic representation partially in cross-section of the apparatus of FIGURE 1 with additional means for controlling the temperatures within the apparatus, and

FIGURE 4 is a perspective view of a gas-cooled shaping guide.

With reference to FIGURE 1, apparatus is shown having an enclosed cylindrical chamber 10 into which bar stock of purified semiconductor 11, such as silicon, is continuously fed through an opening in the bottom thereof. The opening is appropriately fitted with a gas seal 12. An RF heating coil 13 disposed about the central portion of the chamber 10 melts the end of the crystalline bar stock to form a molten mass 14 supported on the end of the bar by its own surface tension. Liquid semiconductor material is withdrawn from melt 14 through a shaping guide 16 which shapes the liquid semiconductor into a thin liquid ribbon 15. The ribbon is then drawn into an inner chamber 17 through an orifice 18 which has substantially the cross-sectional dimensions of the monocrystalline ribbon to be produced. The critical area where the ribbon takes shape in this preferred arrangement is shown in detail in the enlarged view of FIGURE 2.

In the apparatus of FIG. 1, cooling gas enters the chamber 10 through orifice 19. As indicated by the arrows in FIG. 1, the gas passes downward between the walls of chamber 17 and chamber 10 and is forced through the orifice 18 in the inner chamber 17 concurrently with the liquid ribbon 15 passing therethrough. The cooling gas passing through the orifice 18 provides controlled freezing of the liquid semiconductor ribbon into a monocrystalline semiconductor ribbon. As the crystal cross-section increases, the gas flow through the orifice is diminished and the rate of heat transfer from the freezing crystal to the cooling gas diminishes. Consequently, the crystal cross-section is automatically reduced until the gas flow increases. The effect is then reversed. The cooling gas may be any suitable gas which will not contaminate the semiconductor, such as helium or argon, for example.

The monocrystalline semiconductor ribbon 20 is continuously withdrawn from chamber 17 by any suitable means such as rollers 21, 22 and 23 and stored or continuously supplied to a device manufacturing system.

It will be noted that the shape and size of the crystalline

ribbon produced is determined by shaping guide 16 as well as the shape and size of the orifice 18. The shaping guide 16 applies pressure on the liquid supported by surface tension to force the liquid into the form of a thin liquid ribbon. Since the semiconductor is liquid as it passes through the guide 16, the shape of the ribbon is determined by the guide. The guide 16 should present an isothermal rectangular plane through which the liquid semiconductor is drawn so that the melt-solid interface will be rectangular and parallel to the plane of the orifice 18. Shaping guide 16 may be heated or cooled to maintain the necessary isothermal rectangular cross-section for shaping the molten ribbon drawn therethrough.

As depicted in FIGURE 4, the shaping guide 16 may be maintained at any desired temperature by directing a gas stream thereon. As shown in the figure, cooling gas is directed onto the shaping guide 16 by a pair of gas jets 40 to provide an additional control over the thermal gradients in the system. The guide may also be cut into any desired configuration to obtain the desired thermal gradients across the guide.

The guide 16 not only controls the shape of the liquid ribbon by providing an isothermal rectangular cross-section, but also exerts shaping force on the surface of the ribbon. Thus, it is seen that the guide must be made of a material which is not wetted by molten semiconductor, must not contaminate the semiconductor melt, and must not nucleate spurious crystalline growth. Pyrolytic boron nitride has been found to be an acceptable material for the guide when prepared in sufficiently high purity. However, conventional hot-pressed boron nitride contains a binder of boron oxide which tends to contaminate silicon and is consequently unsatisfactory. A dense coating of boron nitride on a refractory metal or other suitable substrate such as graphite may provide a suitable guide which can also be electrically heated if desired. Other materials such as SiN, TiN, ZrN, TaN and other such refractory materials may be also be used if prepared in sufficiently high purity.

The shape of the guide 16 and its heat capacity are important factors in determining the temperature of the liquid ribbon drawn therethrough. The guide should be shaped to uniformly conduct heat from the aperture in its center so that the temperature at the periphery of the aperture is maintained uniform. Thus the guide presents an isothermal rectangular plane which determines the temperature of the semiconductor material drawn therethrough by uniformly extracting heat from the liquid ribbon.

In FIGURE 3, a guide 32 of the preferred shape is shown. The guide 32 is a circular disc of pyrolytic boron nitride with a centrally located slot. The bottom of the disc has a centrally recessed area which aids in guiding liquid material from the top of the liquid semiconductor material into the slot.

The flow of gas through the orifice 18 provides further control over the shape of the semiconductor ribbon. Since the ribbon does not contact the walls of the orifice 18, any suitable material, such as quartz, may be used for the inner chamber 17. As the liquid ribbon 15 is drawn into the orifice 18, cooling gas passing between the walls of the orifice and the liquid ribbon removes heat from the ribbon, thereby causing it to crystallize. The gas flow through orifice 18 provides a second isothermal rectangle through which the ribbon is drawn. This isothermal rectangle is maintained at the freezing point of the semiconductor ribbon; thus the ribbon crystallizes as it passes through orifice 18 and becomes solid ribbon 20. The two isothermal rectangular planes provide a controlled temperature zone having a gradient in which the liquid ribbon from the guide 32 is gradually cooled to its freezing point. The melt-solid interface is parallel to the rectangular isothermal planes of the aperture in the shaping guide and the orifice 18. Thus the ribbon freezes uniformly to form a monocrystalline ribbon.

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The flow rate, thermal conductivity, and specific heat of the gas are factors which affect the temperature of the semiconductor ribbon passing through the orifice 18. Mixtures of gases, such as argon-helium mixtures, may be used to provide the desired specific heat and thermal conductivity at any specified flow rate. Forming gas may also be used to give the additional advantage of a reducing atmosphere within the system.

It will be seen that the initial shaping of the ribbon is provided by the shaping guide 32 and that additional shaping and freezing is provided by the cooling gas passing through the orifice 18 concurrently with the liquid ribbon 15. Accordingly, thin ribbons of monocrystalline semiconductor material of selected thicknesses from about 5 to about 50 mils and varied widths from about 0.1 to about 1 inch may be continuously produced.

The use of a rod or bar stock of feed material provides continuous operation. A suitable mechanical feed mechanism (not shown) can be provided to permit the addition of new rods as the initial rod is consumed in the growing process without interrupting the process. This continuous feed process avoids the use of a melt contained in a crucible, thus avoiding a major source of contamination. Furthermore, conventional heating means, such as RF heating, may be employed to provide a uniformly heated molten region.

Additional means for maintaining control over the temperature within the apparatus are shown in FIGURE 3. The apparatus of FIGURE 3 is similar to the apparatus shown in FIGURE 1 and comprises an enclosed cylindrical chamber 10 into which bar stock of semiconductor material 11 is continuously fed through an opening in the bottom thereof. The opening is appropriately fitted with a gas seal 12. An RF heating coil 13 is disposed about the central portion of the cylinder 10. A concentration coil 33 provides a shaped heat sink which limits the energy from the heating coil 13 to the end of bar stock 11 to form a molten mass 14 of semiconductor material. The molten mass is supported on the end of the bar by its own surface tension.

Liquid semiconductor material is withdrawn from the melt 14 through a shaping guide 32 which shapes the semiconductor material into a thin liquid ribbon. The shaping guide 32 is a circular disc having a centrally located slot or aperture of the shape and size of the cross-sectional dimensions of the desired ribbon. The guide 32 is recessed on the bottom side in the central portion thereof. The recessed region roughly conforms with the curvature of the surface of the liquid mass 14 to aid in guiding liquid material into the slot.

The ribbon is drawn into an inner chamber 17 through an orifice 18 which has substantially the cross-sectional dimensions desired of the monocrystalline ribbon to be produced. Gas flowing through the orifice 18 concurrently with the semiconductor ribbon provides cooling to freeze the ribbon as described above with reference to FIGURE 1.

Heat reflector 34 may be positioned near the liquid ribbon 15 above the shaping guide 32 to further aid in maintaining a uniform temperature gradient. The shape of the ribbon is essentially determined by the aperture in the shaping guide 32, but the temperature of the liquid ribbon 15 must be gradually reduced to allow uniform freezing. Reflector 34 does not contact the liquid semiconductor ribbon, but radiates and reflects thermal energy to the ribbon 15 to maintain a uniform temperature gradient. The reflector may be any suitable refractory material such as that described above for use as a shaping guide.

Auxiliary heaters 31 are disposed about the upper section of chamber 10 to maintain a uniformly decreasing temperature gradient over the semiconductor ribbon. By gradually cooling the ribbon, dislocations and other deleterious effects of thermal shock are avoided.

Pre-heaters 30 may be used to pre-heat the semiconduc-

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tor bar stock 11 prior to melting. The pre-heaters supply sufficient energy to heat the bar 11 to a temperature below its melting point. This provides additional control over the melting end of the bar since the material reaching the melting zone is maintained at a constant temperature. The feed bar stock 11 may also be rotated as it is fed into the chamber 10. Rotating bar 11 assures uniformity of growth from the molten region 14 and uniformity of doping of the ribbon when a doped bar stock 11 is used.

What is claimed is:

1. The method of continuously forming a monocrystalline ribbon of semiconductor material comprising the steps of:

- (a) drawing liquid semiconductor material through an aperture in a shaping guide, said aperture substantially corresponding to the cross-sectional dimensions of the monocrystalline ribbon to be produced;
- (b) drawing said liquid semiconductor material through a second aperture having substantially the cross-sectional dimensions of the ribbon to be produced, and
- (c) passing a cooling gas through said second aperture whereby said gas flows between the sides of said aperture and the semiconductor material, said gas serving to automatically control the size of the monocrystalline ribbon.

2. The method of continuously forming a monocrystalline ribbon of semiconductor material comprising the steps of:

- (a) continuously feeding crystalline bar stock of semiconductor material into a chamber;
- (b) heating the end of said bar stock of semiconductor material to melt a portion thereof, said molten portion being supported on the end of said bar stock by its own surface tension;
- (c) drawing liquid semiconductor material from said molten portion through an aperture, said aperture substantially corresponding to the cross-sectional dimensions of the monocrystalline ribbon to be produced;
- (d) further drawing said liquid semiconductor material through a second aperture having substantially the cross-sectional dimensions of the ribbon to be produced, and
- (e) concurrently passing a cooling gas through said second aperture whereby said gas flows between the sides of said second aperture and the semiconductor material, said gas serving to automatically control the size of the monocrystalline ribbon.

3. In the process of forming monocrystalline ribbon of silicon by withdrawing a ribbon of liquid silicon from a mass of molten silicon, the steps of:

- (a) shaping the liquid ribbon by drawing said liquid through an aperture having dimensions substantially corresponding to the cross-sectional dimensions of the monocrystalline ribbon to be produced;
- (b) drawing said liquid ribbon through a second aperture having dimensions substantially corresponding to the cross-sectional dimensions of the monocrystalline ribbon to be produced, and
- (c) concurrently forcing a gas through said second aperture between the sides of said aperture and the ribbon thereby to further shape said ribbon.

4. The method of claim 1 wherein a controlled isothermal zone is maintained about said ribbon by a controlled flow of gas over the surface of said ribbon.

5. The method of claim 4 wherein said controlled isothermal zone is at least partially maintained by radiation of heat from a reflector positioned adjacent said ribbon.

6. In a crystal growing apparatus of the type adapted to grow a crystal of semiconductive material from a melt of the same, means for continuously advancing bar stock of purified semiconductor material into said apparatus, means serving to melt the end of said bar, a shaping guide having a first aperture therein of the cross-sectional shape and size of the crystalline ribbon to be produced, an inner chamber having a second aperture therein positioned

adjacent said shaping guide so that liquid material drawn through said shaping guide may be drawn directly into said second aperture, means for concurrently forcing a cooling gas through said second aperture, and means for continuously withdrawing a crystalline semiconductor ribbon from said second chamber.

7. The apparatus of claim 6 wherein said shaping guide is a refractory metal having a coating of polished silicon carbide.

8. The apparatus of claim 6 wherein said shaping guide is a refractory metal having a coating of boron nitride.

9. The apparatus of claim 6 wherein there is also provided means for maintaining the temperature uniform at the periphery of said first aperture.

10. The apparatus of claim 6 wherein there is provided a heat reflector positioned adjacent the liquid semiconductor ribbon drawn through said first aperture.

11. The method of continuously forming a ribbon of monocrystalline semiconductor material comprising the steps of:

- (a) continuously feeding a purified bar of said semiconductor material into a chamber;
- (b) heating the end of said bar to melt a portion thereof, said molten portion being supported on the end of said bar by its own surface tension;
- (c) drawing the liquid semiconductor material from said molten portion through a shaping guide which shapes said liquid semiconductor material into the form of a noncircular ribbon by physical contact with said liquid semiconductor material;
- (d) maintaining the temperature of said liquid semiconductor material above the freezing point of said semiconductor material while within said shaping guide;

(e) establishing an isothermal gradient at and above said shaping guide and drawing said ribbon of semiconductor material thereinto;

(f) freezing said semiconductor ribbon in said isothermal zone in free space unconstrained by physical barriers and in a manner which effects a planar freezing zone that is substantially parallel with said shaping guide; and

(g) continuously removing, during formation of said ribbon, said ribbon of semiconductor material which has been frozen.

12. The method of claim 11 wherein said semiconductor material is silicon.

13. The method of claim 11 wherein the establishing of the isothermal temperature zone of step (e) is effected by heat from the molten portion of said bar, by cooling of said shaping guide, and by employing a heat shield completely surrounding said ribbon of molten semiconductor material to retard radiation loss of heat and to effect uniform transfer of heat therefrom.

References Cited

UNITED STATES PATENTS

3,002,821	10/1961	Haron.	
3,124,489	3/1964	Vogel et al.	
3,157,472	11/1964	Kappelmeyer et al.	
2,927,008	3/1960	Shockley	148—1.6
3,291,650	12/1966	Dohmen et al.	148—1.6

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