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PATENT SPECIFICATION 1,102,989

DRAWINGS ATTACHED.

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COMPLETE SPECIFICATION.

Method and Apparatus for Producing Crystalline Semiconductor Ribbon.

We, TEXAS INSTRUMENTS INCORPORATED, a Corporation organised according to the laws of the State of Delaware, United States of America, of 13500 North Central Expressway, Dallas, Texas, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This 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 reduction. 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 usually operates with a precision of about ±0.01°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

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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 disburb the critical thermal gradients and terminate growth, thus limiting the total length of ribbon which can be grown to the batch size.

In accordance with the present invention, a method of continuously forming a monocrystalline ribbon of semiconductor material, comprises feeding a solid rod of semiconductor material axially upwardly into a first chamber, passing the rod progressively into a localized heating zone in the first chamber in which zone successive portions of the solid rod are changed into a liquid state, the liquid semiconductor material in the heating zone being confined laterally of the rod solely by its own surface tension, drawing liquid semiconductor material from the heating zone through an aperture in a shaping guide disposed in the first chamber, the shaping guide aperture extending therethrough for receiving the semiconductor material and having a shape and size substantially corresponding to the cross sectional shape and size of the ribbon to be formed, whereby the semiconductor material is formed into a ribbon upon passing through the shaping guide aperture, and drawing the semiconductor material continuously from the shaping guide into a second chamber while simultaneously passing a cooling gas into the second chamber, the second chamber having a wall portion defining an inlet aperture for receiving the semiconductor material and cooling gas, the inlet aperture in the second chamber having a shape and size substantially corresponding to the cross sectional shape and size of the ribbon to be formed, the cooling gas flowing between the ribbon of semiconductor material and the wall portion of the second chamber defining the inlet aperture, and the cooling gas serving to solidify the ribbon, to prevent the ribbon from contacing the wall portion, and automatically to control the size of the ribbon of semiconductor material. This method can be used to produce monocrystalline material in thin ribbon form which may be directly used for fabricating semiconductor devices without further processing. The invention also provides an apparatus operable to carry out the above method to shape liquid semiconductor material into a thin ribbon and to control the temperature of the ribbon to form 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. The confinement of the molten semiconductor material laterally of the rod by its own surface tension eliminates contamination which might otherwise occur if the molten semiconductor material contacted wall portions of a containing vessel. 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 prevent contamination of the semiconductor material from the walls of the orifice by preventing contact therebetween, and 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 features and advantages of the invention 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 guides,

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, so as to eliminate contamination which might otherwise occur if molten semiconductor material contacted wall portions of a containing vessel. 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 FIGURE 1, cooling gas enters the chamber 10 through orifice 19. As indicated by the arrows in FIGURE 1, the 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 prevents contamination of the semiconductor material from the walls of the orifice by preventing contact therebetween, and also 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, less semiconductor material crystallizes as it is being drawn and the crystal cross-section is automatically reduced. This results in an increase in gas flow, an increase in the rate of heat transfer, an increase in the amount of semiconductor material crystallizing as it is being drawn, and an increase in the crystal cross-section. The cycle is then ~~reseated~~ repeated, and the crystal cross-section automatically controlled within close limits. 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 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.

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 soil 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 ~~gradiant~~ gradient. The shape of the ribbon is essentially determined by the aperture in the shaping guide 32, but the temperature of the liquid ribbon 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 semiconductor 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 is used.

Although the invention has been described with reference to the preferred embodiments thereof, it is to be understood that the forms of the invention herewith shown and described are to be taken as the preferred embodiment of the same, and that various changes may be resorted to without departing from the scope of the invention as defined by the appended claims.

WHAT WE CLAIM IS: —

1. A method of continuously forming a monocrystalline ribbon of semiconductor material, comprising feeding a solid rod of semiconductor material axially upwardly into a first chamber, passing the rod progressively into a localized heating zone in the first chamber in which zone successive portions of the solid rod are changed into a liquid state, the liquid semiconductor material in the heating zone being confined laterally of the rod solely by its own surface tension, drawing liquid semiconductor material from the heating zone through an aperture in a shaping guide disposed in the first chamber, the shaping guide aperture extending therethrough for receiving the semiconductor material and having a shape and size substantially corresponding to the cross sectional shape and size of the ribbon to be formed, whereby the semiconductor material is formed into a ribbon upon passing through the shaping guide aperture, and drawing the semiconductor material continuously from the shaping guide into a second chamber while simultaneously passing a cooling gas into the second chamber, the second chamber having a wall portion defining an inlet aperture for receiving the semiconductor material and cooling gas, the inlet aperture in the second chamber having a shape and size substantially corresponding to the cross sectional shape and size of the ribbon to be formed, the cooling gas flowing between the ribbon of semiconductor material and the wall portion of the second chamber defining the inlet aperture, and the cooling gas serving to solidify the ribbon, to prevent the ribbon from contacting the wall portion, and automatically to control the size of the ribbon of semiconductor material.

2. A method as claimed in claim 1, in which the liquid semiconductor material drawn through the first aperture is formed by melting the end of a rotating bar of semiconductor material.

3. A method of continuously forming a monocrystalline ribbon of semiconductor material, substantially as described herein with reference to the accompanying drawings.

4. Crystal-growing apparatus of the type adapted to grow a crystal of semiconductor material from a melt of same, having means operable to advance continuously bar stock of purified semiconductor material into an aperture, means operable to melt the end of the bar and a shaping guide having an aperture therein having cross-sectional shape and size substantially corresponding to that of the crystalline ribbon to be produced, an inner chamber having a chamber aperture therein positioned adjacent the shaping guide so that liquid material drawn through the shaping guide can be drawn directly into the chamber aperture, means operable concurrently to force cooling gas through the chamber aperture, and means operable continuously to withdraw a crystalline semiconductor ribbon from the inner chamber.

5. Apparatus as claimed in claim 4, including means to cool the shaping guide in the area of its aperture.

6. Crystal growing apparatus substantially as described herein with reference to and as illustrated by the accompanying drawings.

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