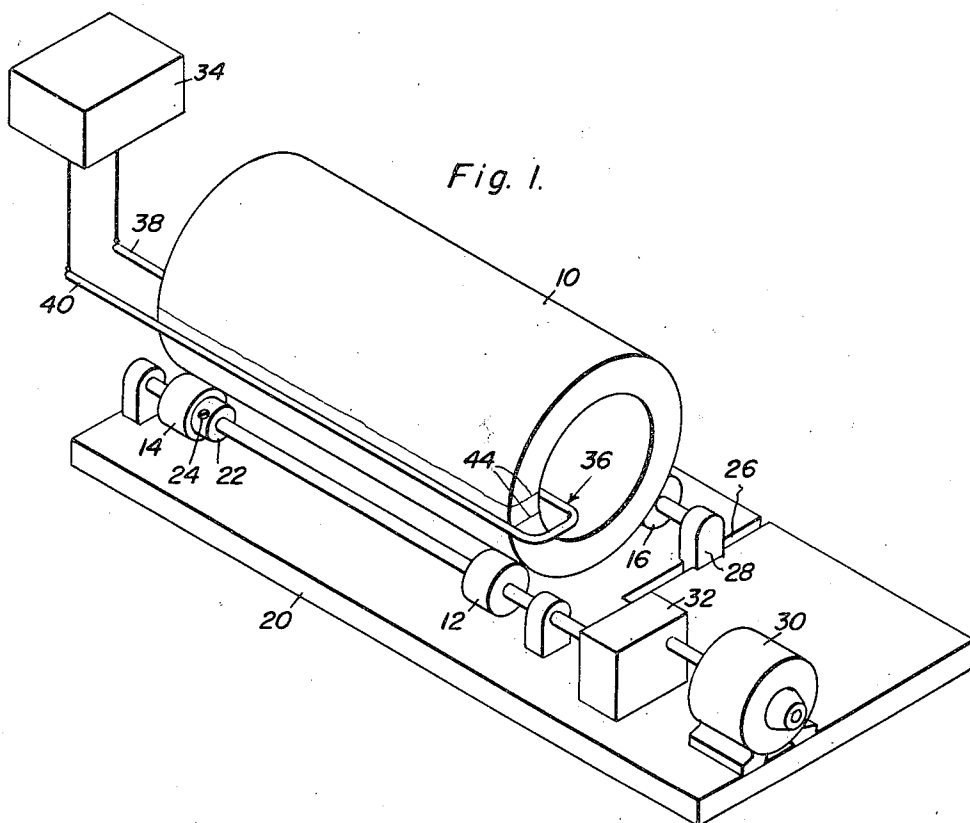
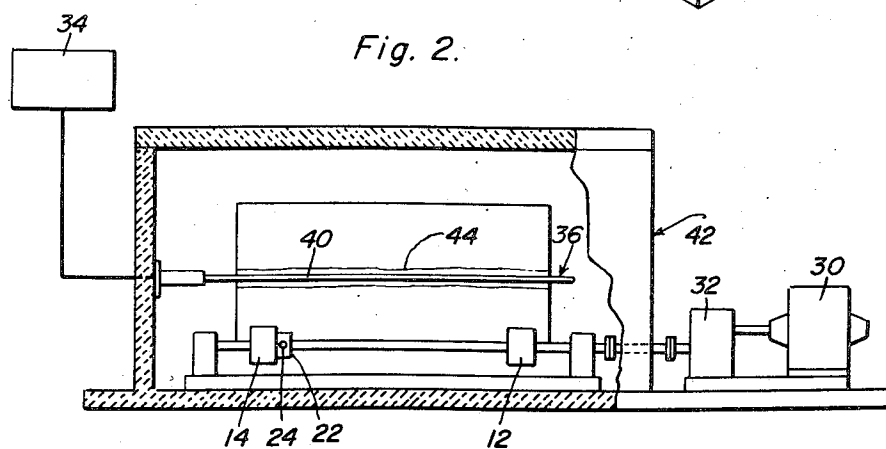


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METHOD AND APPARATUS FOR FORMING SINGLE
CRYSTAL IN CYLINDRICAL FORM
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1

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METHOD AND APPARATUS FOR FORMING SINGLE CRYSTAL IN CYLINDRICAL FORM

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This invention relates to forming single crystals of metal in cylindrical form, and, more particularly, to a method and apparatus employed to form a single crystal cylinder from polycrystalline cylinders of silicon.

Commercially produced semiconductor grade silicon is generally available in two forms. One form consists of chips, broken bits, or flakes and is characteristic of the zinc vapor reduction of silicon tetrachloride. The other form is a smooth rod of uniform diameter, normally monocrystalline and usually prepared by the thermal decomposition of silane, SiH_4 , or by hydrogen reduction of trichlorosilane, SiHCl_3 . In the manufacture of transistors, diodes, rectifiers, and the like, the single crystal rod form is preferably employed because of the added purification resulting from the single crystal growth, and the fact that handling and transportation techniques do not degrade the purity as occurs in handling or transporting the chip or flake form.

A particular disadvantage of the rod form of silicon is the smallness of the unit of manufacture. For example, the commercially obtainable rod size is approximately $\frac{5}{8}$ inch diameter, 14 inches long and of generally less than $\frac{1}{2}$ pound. To provide greater quantities of these rods, a larger number of preparing units would be required with attendant rise in cost of equipment and labor. If, on the other hand, the equipment ordinarily used were so used to prepare larger single quantities, for example, 3 to 10 pounds each, a considerable efficiency and cost reduction would be obtained if the purity level were maintained.

In my copending application, Serial No. 751,088, assigned to the same assignee as the present invention and filed concurrently herewith, there is disclosed and claimed a method of decomposing or reducing a silicon compound on a heated silicon surface quartz or tantalum surface form solid silicon of improved purity. By the use of this method, a silicon deposit may be obtained in excess of one pound and a deposit which is characterized by being of exceptional purity, dense, solid, regular shaped, free of cracks, and tubular or cylindrical if desired. Such a deposit also is larger than the approximate $\frac{1}{2}$ pound rods now generally available. For example, a cylinder of 8 inches outside diameter, $\frac{6}{8}$ inches inside diameter and 8 inches long will contain approximately 10 pounds of silicon. The cylindrical form of silicon is readily adaptable for cutting to obtain an annulus, rectangular rods and other geometric forms which are preferred in various silicon applications. These forms, however, are more preferred in single crystals. Previously, the aforementioned chip or flake variety of silicon required melting to rod form and added purification by zone refining or float leveling. Therefore, since the process of the above copending application provides a substantially improved purity cylinder of silicon, a simple conversion of the polycrystalline cylinder to a single crystal cylinder, the problems of cost, efficiency, desirable form, purity, and availability are substantially overcome.

Accordingly, it is an object of this invention to provide means for producing single metal crystal cylinder from a polycrystalline cylinder.

2

It is another object of this invention to provide a method and apparatus to produce a single crystal silicon cylinder from a polycrystalline cylinder.

It is a further object of this invention to provide a single crystal silicon cylinder of improved purity.

Briefly described, this invention in one form includes forming a single crystal silicon cylinder from a polycrystalline silicon cylinder by a controlled method of melting a predetermined area of the cylinder, and progressively melting additional and adjacent portions of the cylinder while the former molten portions solidify. The process includes this treatment as applied to the total surface of the cylinder by an apparatus which not only supports and rotates the cylinder but also adds no impurities to the silicon.

This invention will be better understood when taken in connection with the following description and the drawing, in which:

Fig. 1 is a schematic illustration of the apparatus employed in this invention and

Fig. 2 is a modified view of the apparatus of Fig. 1 positioned within an enclosure or furnace.

Referring now to Fig. 1, there is shown a silicon cylinder 10 which may be formed by various processes including the thermal decomposition of silicon tetraiodide on a heated cylindrical surface, or merely a cylinder formed from available silicon. In any event, it is contemplated that cylinder 10 be of substantially pure silicon with no particular foreign ingredient therein. Cylinder 10 is mounted on a roller bed arrangement illustrated by four roller elements 12, 14, 16, and 18, each of which is mounted for rotation upon a base 20. Case should be taken in the choice of materials for the rollers so that the material thereof adds no impurities to cylinder 10 undergoing treatment. While tantalum and quartz may be employed in the preferred form of this invention the rollers are quartz and coated with a silicon dioxide film according to the teaching of my copending application, Serial No. 751,089, assigned to the same assignee as the present invention and filed concurrently herewith. That application discloses coating quartz and tantalum surfaces with SiO_2 by exposure to the products of combustion of silicon tetraiodide, burned in precleaned air together with small amounts of hydrogen. Other film coatings that constitute an effective diffuser barrier to the addition of impurities to the silicon may also be employed.

Alternatively suitable apparatus may be employed in this invention to continually coat the rollers during operation. With the cylinder 10 resting upon the four rollers, it is understood that when rotational energy is provided to one or more of the rollers, they will in turn rotate the cylinder 10, and that the speed of rotation is easily determined by the ratio of the diameter of the rollers to the diameter of the cylinder. The rollers are made adjustable to provide for mounting cylinders 10 of varying lengths and diameters. An exemplary method of longitudinal adjustment is shown associated with roller 14, the same being applicable for roller 18, not shown. Roller 14 includes a collar 22 with a set screw 24 therein, the combination permitting roller 14 to be positioned along its shaft. A lateral adjustment arrangement in the form of a keyway 26 is shown associated with roller 16 and which is also applicable to roller 18, not shown. The mounting base 28 for roller 16 is slidably positioned in track or keyway 26 for various diameter cylinders. In one form of this invention, a suitable variable speed electric motor 30 combined with a speed reducing device 32 is employed to drive rollers 12 and 14.

Particularized area heating is obtained by means of an RF induction heater illustrated schematically as 34 and an elongated hairpin type of induction heater coil 36. Coil 36 is best described as having two legs 38 and

40 of one or more turns and positioned in relation to the silicon cylinder 10 so that one leg 38 is longitudinally inserted within cylinder 10 to lie adjacent the inner surface, while the other leg 40 is positioned longitudinally outside the cylinder to lie adjacent the outer surface with the two legs in a generally horizontal and central plane. It is understood that coil 36 may also be modified or changed to further provide for cylinders 10 of various thicknesses, lengths, and diameters.

In order to carry out the method of this invention, the apparatus of Fig. 1 is shown in Fig. 2 as positioned within a suitable enclosure or furnace 42.

In Fig. 2, furnace 42 is adaptable for temperature operation, inert atmospheres, or vacuum. The inert atmosphere, for example, may be hydrogen, argon, helium, or other gas which will not add or provide impurities to cylinder 10. However, it may be desirable to add a minor material or ingredient to the cylinder 10. In the instance of the cylinder 10 being silicon, and for example, if boron were to be added, a small amount of diborane or other boron component which is volatile under the operating conditions may be introduced into the furnace. Generally speaking, there is introduced into furnace 42, a hydride of the particular metal desired to be added to cylinder 10. The particular method or apparatus for evacuation of, or the introduction of an inert atmosphere is of no importance to this invention and is well known in the prior art.

With the arrangement as shown in Figs. 1 and 2, the induction heater 34 or other form of heat energy is applied to melt a narrow, longitudinal section 44 of cylinder 10. The coil 36 is positioned horizontally and substantially centrally with respect to the vertical dimension of cylinder 10. Such an arrangement provides a two-fold support in that, first, the unmolten portion of the cylinder is self-supporting and does not rest upon the molten section 44, and second, the molten section 44 need not support its total weight as the case would be if the section 44 were at the bottom of the cylinder. While the molten silicon has a surface tension sufficiently high with respect to its own thickness and height so that no loss of metal is encountered when practicing this invention, a plurality of such sections would head to silicon flow or collapse of cylinder 10.

After the molten condition of the section is established, the silicon cylinder is slowly rotated so that a section adjacent the molten section progresses to the molten condition while the aforementioned molten section progressively solidifies. An overall description of such a process may be described as saying that the silicon cylinder 10 is rotating while the molten zone 44 remains stationary.

When the rotation of the cylinder 10 is maintained within prescribed limits, the molten silicon solidifies at the following edge of the molten zone and will soon become a single crystal as the lattice with the most favorable orientation will crowd out the others. After a few rotations, the entire cylinder will be a single crystal and the process has eliminated the need for a seed crystal in starting the process.

The crystal growing process just described has subjected the cylinder to substantial purification. With the molten zone 34 including a length of the cylinder, and with unidirectional continual rotational motion which repeatedly passes the same zone of the cylinder, there will be an averaging of the impurity gradient, a process commonly referred to as "zone leveling." The single crystal thus formed has an impurity concentration which is constant radially, circumferentially, and longitudinally, except for a single longitudinal element which solidifies last in the process. The last zone to solidify contains most of the impurities and may be removed from the cylinder.

It is understood that the general practicing procedure of this invention is quite dependent on the general size of the silicon cylinder. Useful results are most readily obtained when the cylinder is about 4 inches in diameter

with a wall thickness in the approximate range of $\frac{1}{2}$ to 1 inch. The temperature of the molten zone of the cylinder is maintained at about 1420° C. combined with a rotation of the cylinder of about 2 inches per hour.

The single crystal cylinder of this invention may be fractured or otherwise cut for use in semiconductor devices or into rod-like elements for further purification. Such a cylinder finds good application as a cylindrical surface for the processes of silicon manufacture utilizing the thermal decomposition or reduction of silicon compounds, upon which silicon is deposited or formed.

This invention is equally applicable to the preparation of high purity iron, titanium, zirconium, tungsten, and other metals and semi-conductors having required melting points and sufficient surface tension in the molten condition.

There has thus been described, a method together with a particular apparatus to provide a substantially pure single crystal silicon cylinder. The apparatus provides a novel supporting arrangement for rotating cylinders to permit the practice of the method thereon.

While other modifications of this invention and variations of apparatus which may be employed within the scope of the invention have not been described, the invention is intended to include all such as may be embraced within the following claims.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. The method of growing a single crystal cylinder from a polycrystalline cylinder which comprises, maintaining the cylinder in a substantially horizontal plane, providing a controlled atmosphere about the cylinder, providing non-contaminating support for said cylinder, supporting the cylinder for rotation, reducing a single longitudinal horizontal section of the cylinder to the molten condition where the molten section does not support its own weight and the remainder of the cylinder is self-supporting, slowly rotating the cylinder while maintaining the molten section stationary and in the horizontal plane and repeating the process until a single cylindrical crystal is formed.

2. The method of growing a single crystal cylinder of silicon from a polycrystalline cylinder which comprises, maintaining the cylinder in a substantially horizontal plane, providing a controlled atmosphere about the cylinder, providing non-contaminating support for said cylinder, supporting the cylinder for rotation reducing a longitudinal horizontal section of the cylinder to the molten condition where the molten section does not support its own weight and the remainder of the cylinder is self-supporting at a temperature about 1420° C., slowly rotating the silicon cylinder while maintaining the molten section stationary and in the horizontal plane at a speed of approximately 2 inches per hour, and repeating the process until a single cylindrical crystal is formed.

3. An apparatus for growing a single crystal silicon cylinder from a polycrystalline cylinder which comprises in combination, a furnace enclosure means to support a cylinder in a substantially horizontal plane in said furnace, said support means including supporting elements the material of which is inert with respect to silicon, means to heat a single narrow longitudinal section of said cylinder to reduce the section to a molten condition where the molten section does not support its own weight and the remainder of the cylinder is self-supporting, and means to rotate said cylinder to reduce adjacent narrow sections to the molten condition while permitting the molten section to solidify.

4. An apparatus for providing a silicon single crystal cylinder of substantial purity from a polycrystalline cylinder which comprises, a base member, a plurality of roller members rotationally mounted on said base to provide a substantially horizontal and rotating support for a silicon cylinder, said roller material being characterized as being substantially inert with respect to silicon, an induction

5

heater connected to a source of power, an induction coil connected to said heater, said coil being positioned with one leg longitudinally within said cylinder and another leg longitudinally without said cylinder in a central horizontal plane, means to provide current and voltage to said coil to reduce a longitudinal horizontal section of said cylinder to the molten state, means to maintain a controlled atmosphere about cylinder and means to rotate said cylinder while maintaining the molten state between the said legs of said coil.

5. The invention as claimed in claim 4 wherein said rollers are tantalum.

6. The invention as claimed in claim 4 wherein said rollers are quartz.

6

7. The invention as claimed in claim 4 wherein said rollers are coated with a film of SiO_2 .

References Cited in the file of this patent

UNITED STATES PATENTS

2,739,088	Pfann	Mar. 20, 1956
2,890,940	Pfann	June 16, 1959
2,895,813	Brooksbank	July 21, 1959

OTHER REFERENCES

Pfann: Zone Melting, March 1958, pp. 64, 65, 89 and 148.