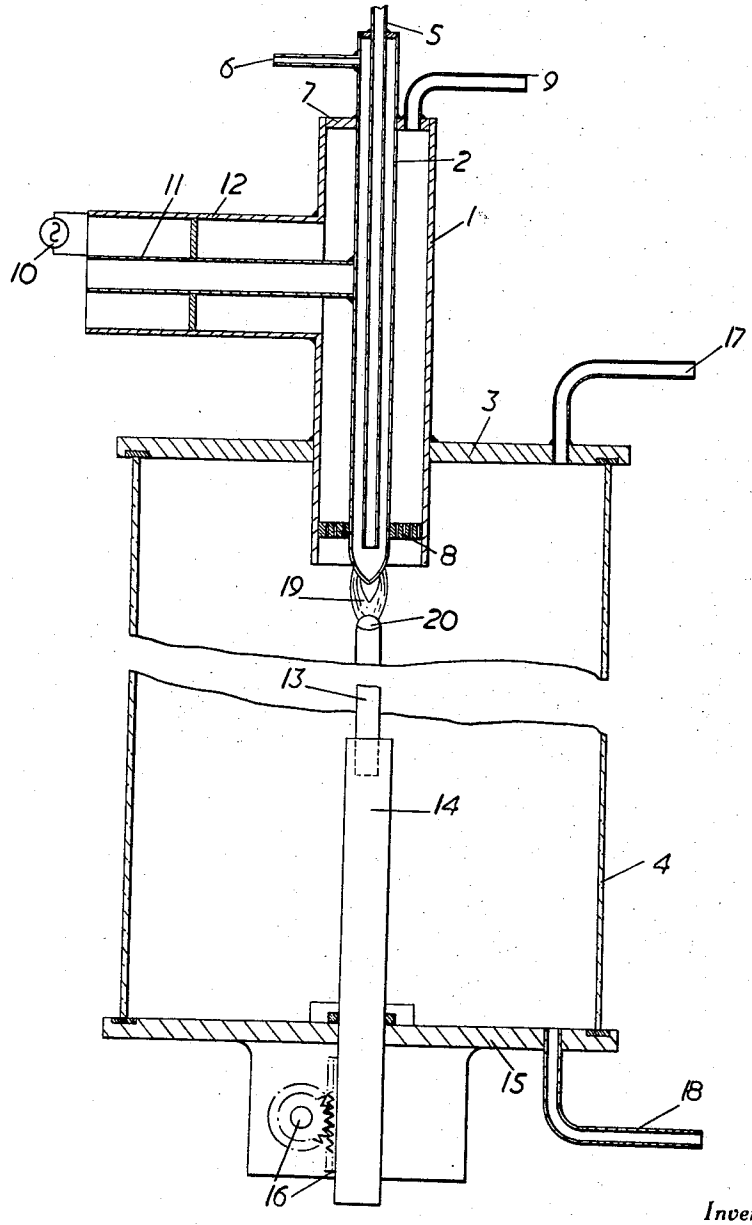
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MANUFACTURE OF SEMICONDUCTOR MATERIAL

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# MANUFACTURE OF SEMICONDUCTOR MATERIAL

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This invention relates to the manufacture of semiconductor material and has for its object to produce such material of high purity.

It has been proposed in British patent specification No. 745,698 to manufacture substantially pure silicon by passing substantially pure silane in a molecular concentration substantially less than normal into a zone heated to a temperature at least equal to the decomposition temperature of silane. This method of manufacture has proved successful in producing silicon of such a high degree of purity, that no impurities are detectable spectrographically. Monocrystalline silicon can be produced by this process but the rate of growth of a body of such silicon is slow so that it is preferred to produce at a faster rate a polycrystalline body which is afterwards converted into a monocrystal by melting and pulling a crystal from the melt. In order to avoid contamination from a crucible it is preferred to pull the monocrystal by means of the method and apparatus described in U.S. application No. 688,460, filed October 7, 1957.

The monocrystal is in the form of a rod and there are some limitations upon the diameter of the monocrystalline rod produced either by this method or by the previously known method of pulling from a melt in a crucible.

In British Patent No. 778,383, it has been proposed to manufacture other semi-conductor material, such as germanium, by thermal decomposition of the corresponding hydride.

It is the object of the present invention to manufacture semi-conductor material of a very high degree of purity at a faster rate than that achieved by the methods above referred to.

The method according to the present invention involves the decomposition of a hydride of the semi-conductor material that can be obtained free from contamination by compounds of impurity elements.

According to the present invention a gaseous hydride of the semi-conductor element is passed through a zone in which it is decomposed by means of electro-magnetic energy applied to the gas. On leaving this zone, association of some of the atoms in the said gaseous compound takes place with the liberation of energy, which is sufficient to melt the semi-conductor material.

The invention will be better understood from the following description of one form of apparatus for carrying out the invention, taken in conjunction with the accompanying drawing.

Referring to the drawing, there is shown in section an apparatus for the manufacture of pure silicon. The outer conductor **1** of a coaxial transmission line **1**, **2** for high frequency electromagnetic energy is sealed through the upper closure plate **3** for a cylinder **4** of silica. The coaxial transmission line **1**, **2** is preferably made of silver and the inner conductor **2** consists of a hollow tube. Water is circulated through the inner conductor **2** by means of an inlet pipe **5** extending down the interior of hollow conductor **2** and an outlet pipe **6** branched from conductor **2** near the end thereof remote from the end



of inlet pipe **5**. The end of inner conductor **2** which protrudes through plate **3** is closed as shown to allow of such water circulation. The inner and outer conductors **1**, **2** are held in spaced relation by washers **7**, **8** of polytetrafluorethylene. The washer **7** seals the space between inner and outer conductors **1** and **2** except for a pipe **9** through which silane gas enters the space between inner and outer conductors, whilst the washer **8** is provided with orifices through which silane gas can pass.

Radio frequency power is supplied to the coaxial transmission line **1**, **2** from a generator, shown diagrammatically at **10** connected between inner and outer conductors **11**, **12** of a feeder coaxial transmission line connected to the line **1**, **2** one quarter wave length from that end of the line **1**, **2** closed by the washer **7**. This power may be of a frequency between ½ mc./s. and 1000 mc./s., preferably between 500 and 1000 mc./s. A suitable power is 5 kw. The length of the transmission line is made such that the first voltage anti-node occurs at or near that end of the transmission line **1**, **2** that is within the cylinder **4**.

A rod **13** of silicon is mounted on a support **14** that is sealed through a bottom closure plate **15** for the cylinder **4** in such a manner that it is capable of longitudinal movement. Gearing **16** is provided for effecting such movement. A protective gas such as argon enters the cylinder **4** through inlet pipe **17** and leaves through outlet pipe **18**.

In operation the silane which flows through the space between inner and outer conductors is decomposed at the anti-node of the coaxial transmission line into silicon and atomic hydrogen. Immediately beyond this point the atoms of hydrogen recombine into molecules with evolution of heat, forming an electrodeless flame discharge **19** which melts the silicon resulting from the decomposition of the silane. The rod **13** is placed so that its upper end is in the region of the discharge and is melted thereby to form a pool **20** of molten silicon. The silicon resulting from this decomposition is deposited on this molten pool.

As further silicon is deposited the rod **13** is gradually lowered and the silicon previously deposited solidifies.

Although the silicon mounted on the support **14** is shown as a rod **13** it is to be understood that this is the condition after the process has been in operation for some time. Initially only a seed of silicon is mounted on support **14**. If this seed be a monocrystal the rod **13** may be grown as a monocrystal by suitable regulation of its rate of growth. By means of the apparatus and method described it is possible to grow a rod of monocrystalline silicon having a diameter in excess of 2.5 cm. and the growth rate is greater than can be achieved by the method according to British Patent No. 745,698 and is as great as can be achieved by a crystal "pulling" technique.

The vessel **4** is filled with argon which provides a protective atmosphere preventing oxidation of the growing crystal.

The invention is applicable to the manufacture of any semi-conductor elements having volatile hydrides such as silicon, germanium, boron &c. By semi-conductor element is meant an element which is (*a*) semi-conductive when alone or (*b*) will produce a semi-conductive material when in combination with another element.

For the manufacture of germanium the hydride may be used in the same manner as silane in the manufacture of silicon. Boron, phosphorus, arsenic and/or antimony may be used to confer on silicon or germanium semiconductor properties of a particular type N or P and are, therefore, preferably manufactured as thin layers in a monocrystal of silicon or germanium. For example N-type germanium or silicon is produced by replacing silane in the example above quoted by a mixture in suitable proportions of silane and diborane, or a mixture of

germanium hydride and diborane. The flow of the mixture through the high frequency field is continued only for sufficient length of time to produce the required amount of N-type material. This flow is then succeeded by a flow of silane or germane as the case may be if intrinsic silicon or germanium is to be produced, or by a flow of silane or germane mixed in the required proportion with phosphine, if P-type material is to be produced.

Successive layers of N and P type material or of N, intrinsic and P type material may be produced in this manner throughout the body of semi-conductor monocrystal grown.

In any process according to the invention the temperature produced in the flame may be reduced by mixing a monatomic gas such as argon with the gaseous hydride, and thus reducing the degree of disassociation and subsequent re-association that takes place. For this purpose the flow of argon through the cylinder 4 may be regulated.

Mixture of another gas with the gaseous hydride reduces the amount of semi-conductor solid produced for a given volume of gas, and a reduction of the amount of semi-conductor solid produced may be necessary, in the case of production of mono-crystalline material, to ensure a rate of growth compatible with the production of a single crystal.

The gaseous hydride such as silane used in this process may be mixed with hydrogen if it be found necessary to slow down the rate of production of the solid semi-conductor material without reducing the temperature in the flame, and thus in this case a mixture of hydrogen and silane is fed through pipe 9.

Any such added hydrogen must be in pure condition to avoid any possible introduction of impurities into the semi-conductor material.

While the principles of the invention have been described above in connection with specific embodiments, and particular modifications thereof, it is to be clearly understood that this description is made only by way of example and not as a limitation on the scope of the invention.

What I claim is:

1. Method of manufacturing a semi-conductor element which comprises flowing a gaseous hydride of said element past a voltage anti-node in an electrical high frequency transmission line whereby the hydride is decomposed into the element and atomic hydrogen, melting the semi-conductor material by heat produced by the recombination of hydrogen atoms resulting from such decomposition and collecting the molten element.

2. Method as claimed in claim 1 in which the semiconductor element is silicon.

3. Method as claimed in claim 1 in which the said high frequency transmission line is a coaxial transmission line having separated outer and inner conductors which comprises feeding said line with electromagnetic energy of a frequency between ½ mc./s. and 1000 mc./s., terminating said line near a voltage anti-node, flowing said gaseous hydride through the space between said inner and outer conductors, and collecting the molten element upon a seed body within the flame produced by the said recombination of atoms of hydrogen.

4. Method as claimed in claim 3 comprising also the step of withdrawing the said seed body with the deposited molten material at a rate commensurate with the rate of deposition of molten material.

5. Method as claimed in claim 4 in which said seed body is a monocrystal.

6. Method of manufacturing a monocrystalline body of an element chosen from the class consisting of silicon and germanium which comprises decomposing a gaseous hydride of said element at a voltage node of a high frequency electrical transmission line supplied with suitable electrical power, melting the semiconductor material by heat produced by the recombination of hydrogen atoms resulting from such decomposition, depositing the molten semiconductor element upon a monocrystalline seed of the same element and withdrawing the seed with the deposited material from the molten zone to allow solidification of the molten material as a monocrystal.

7. Method as claimed in claim 6 of manufacturing a monocrystalline body having successive N and P regions therein which comprises successively mixing the hydride of the said element with hydrides of donor and acceptor elements.

8. Apparatus for manufacturing a body of semi-conductor element chosen from the class consisting of silicon and germanium comprising a coaxial electric transmission line having an outer conductor and a hollow inner conductor, means for circulating cooling fluid through said inner conductor, means for applying electrical energy of a frequency between ½ mc./s. and 1000 mc./s. and of suitable power between said inner and outer conductor, means for flowing a hydride of the said semiconductor element through the space between said inner and outer conductors, said conductors being terminated near to a voltage anti-nodal position for said energy, means for locating a seed body at such distance from the said anti-nodal position as to be within the flame produced by recombination of atoms beyond said position, and means for moving said seed body away from said position.

9. Apparatus as claimed in claim 8 in which said anti-nodal position is within a vessel through a wall of which said outer conductor is sealed and means for passing a monatomic gas into and out of said vessel.

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