

[54] **METHOD FOR CRUCIBLE-FREE  
FLOATING ZONE MELTING A  
CRYSTALLINE ROD, ESPECIALLY OF  
SEMI-CRYSTALLINE MATERIAL**

[72] Inventor: **Wolfgang Keller, Pretzfeld, Germany**

[73] Assignee: **Siemens Aktiengesellschaft, Berlin, Germany**

[22] Filed: **Feb. 26, 1969**

[21] Appl. No.: **802,467**

[30] **Foreign Application Priority Data**

Feb. 29, 1968 Switzerland .....2585/68  
May 30, 1968 Switzerland .....8043/68

[52] U.S. Cl. ....65/32, 23/301 SP, 65/33,  
65/86, 65/DIG. 7, 252/500, 252/512

[51] Int. Cl. ....H01j 17/08

[58] Field of Search .....252/512, 500; 23/295, 300,  
23/301 SP, 273; 148/1.6; 65/17, 63, 66, 32, 33, 86

[56] **References Cited**

**UNITED STATES PATENTS**

2,972,525 2/1961 Emeis .....23/301

2,992,311 7/1961 Keller .....23/301 X  
3,157,537 11/1964 Jacob .....148/1.6  
3,223,493 12/1965 Keller et al. ....23/301  
3,265,470 8/1966 Keller .....23/301  
3,342,970 9/1967 Emeis .....23/301 X  
3,351,433 11/1967 Keller .....23/301  
3,442,622 5/1969 Monnier et al. ....148/1.6 X

*Primary Examiner*—John T. Goolkasian

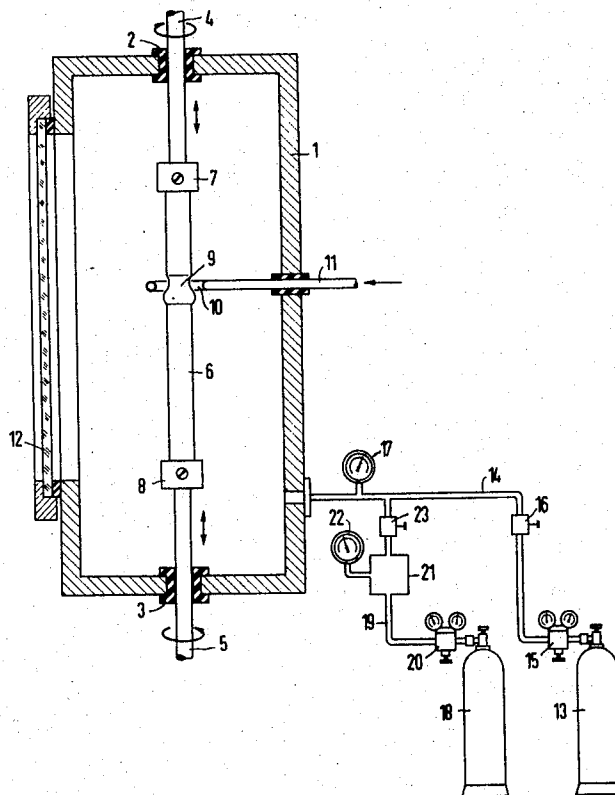
*Assistant Examiner*—Joseph C. Gil

*Attorney*—Curt M. Avery, Arthur E. Wilfond, Herbert L. Lerner and Daniel J. Tick

[57] **ABSTRACT**

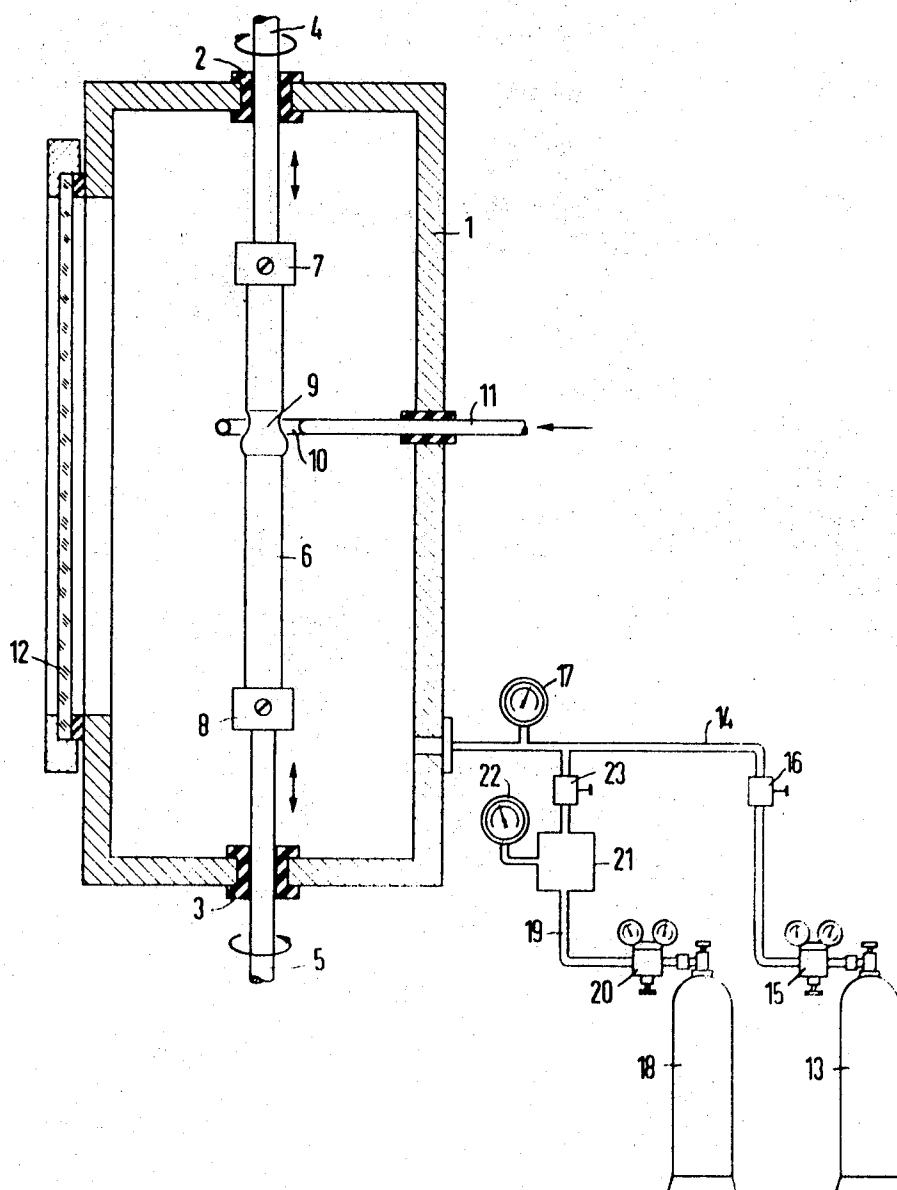
In method of floating zone melting a crystalline rod, especially of semiconductor material, disposed in a sealed receptacle wherein an induction heating coil surrounds the rod and forms a molten zone therein, the rod and heating coil being relatively movable so as to pass the molten zone through the rod, the improvement is provided which comprises passing hydrogen gas of at least 99.9 percent purity into the receptacle so as to form a protective atmosphere therein, and adjusting the pressure of the atmosphere in the receptacle to a value below atmospheric pressure; and device for carrying out the foregoing method.

**10 Claims, 1 Drawing Figure**



PATENTED MAY 2 1972

3,660,062



# **METHOD FOR CRUCIBLE-FREE FLOATING ZONE MELTING A CRYSTALLINE ROD, ESPECIALLY OF SEMI-CRYSTALLINE MATERIAL**

My invention relates to method and device for crucible-free floating zone melting a crystalline rod, especially of semiconductor material. More particularly the device includes a zone melting chamber or receptacle in which there is located a ring-shaped induction heating coil for surrounding the crystalline rod and forming a molten zone therein. A protective gas atmosphere of hydrogen is provided in the receptacle.

It is already known to provide method of producing elongated and especially dendritic semiconductor members by pulling them out of a melt that is subcooled below the melting point of the semiconductor material and, if desired, is doped with selected impurities. The semiconductor melt held in a support formed of the same semiconductor material is accordingly heated by a heating device, and the portion of the melt adjacent the location at which the semiconductor member is being pulled from the melt is subcooled. This heretofore known method is carried out in a sealed chamber or receptacle through which a neutral, preferably reducing gas of relatively good heat conductivity, particularly hydrogen, is passed. The pressure of the hydrogen in the known process is above atmospheric pressure, a requirement necessary to prevent entry of atmospheric air into the receptacle through an opening in the cover of the receptacle through which the dendrite is pulled (note German Pat. DAS 1 162 329).

It is accordingly an object of my invention to provide method and device for floating zone melting a crystalline rod wherein the advantages derived from the use of hydrogen as protective gas are maintained, namely the relatively inexpensive purification thereof, preferably by diffusion through palladium or by freezing the impurities out of the hydrogen, and its slight tendency toward flash-over in a high frequency field. Another object is also to minimize or virtually prevent impurities from contaminating the crystalline rod being processed.

With the foregoing and other objects in view, I provide such method and device wherein highly purified hydrogen is employed and the pressure in the receptacle is adjusted to a value less than atmospheric pressure. More specifically the hydrogen gas employed has a purity of at least 99.9 percent.

In accordance with other features of my invention, the pressure of the hydrogen atmosphere in the receptacle is adjusted to between 30 and 600 Torr. When carrying out the method in an atmosphere whose pressure is maintained within this pressure range, there is assurance that no glow discharge will occur in the high frequency field of the inductive heater. Simultaneously, this pressure range prevents precipitation, for example, of silicon or dopant from the melt, if the latter is formed in a crystalline rod of silicon material. Moreover, within this pressure range, danger of contaminating the crystalline rod being processed is reduced to a minimum since only so much protective gas is admitted to the receptacle as is required to provide the initially mentioned advantages.

To prevent danger of explosion due to the formation of detonating gas by the sudden introduction of air into the hydrogen-filled receptacle, for example through damage to the viewing window in the receptacle, leaks in the receptacle walls, or the like, I provide, in accordance with a further feature of my invention, a further protective gas, preferably a mobile gas, added to the hydrogen. It has been found particularly advantageous to employ argon as the added gas, for example having a purity of 99.995 percent. The protective gas added to the hydrogen should have at least the same degree of purity as that of the hydrogen in order to keep the impurities in the crystalline semiconductor rod as small as possible. A degree of purity of 99.999 percent can also be readily attainable at reasonable cost for the noble gases argon and helium. In spite of its rather greater tendency to flash-over as compared to argon, helium is nevertheless well suited for use as an added protective gas component. Other gases besides the noble gases, namely gases, such as nitrogen for example, that have an inert effect up to a specific partial pressure during practice of the zone melting process, are suited as additive protective gas

components. A particularly well-suited gas mixture is that known as forming gas, which consists of a nitrogen-hydrogen mixture with 80 parts nitrogen and 20 parts hydrogen. It is essential when employing nitrogen as additive protective gas component in a crucible-free floating zone process applied to silicon, that the partial pressure of the nitrogen be at most 100 Torr. When the nitrogen component has a greater partial pressure, there arises the danger of the formation of silicon nitride which jeopardizes the monocrystal growth. To keep the danger of contaminating the semiconductor rod being processed as small as possible, it is advantageous that one or more protective gas components be added to the hydrogen in such quantity that the total pressure in the receptacle is 30 to 600 Torr, and preferably 100 Torr. Very desirable conditions especially with respect to the heating power requirement are obtained when the partial pressure of the additive gas is more than double the partial pressure of the hydrogen. This is caused by the fact that the aforementioned inert gases have a lower heat conductivity than that of hydrogen.

The device employed for carrying out the aforescribed method of my invention comprises a sealed receptacle, end holder means mounted in the receptacle for supporting a crystalline rod therein, induction heating means sealingly extending through a wall of the receptacle into the interior thereof for heating the crystalline rod so as to form a melting zone therein, means for moving the end holder means and the induction heating means relative to one another so as to pass the melting zone axially along the crystalline rod, gas inlet means formed in the wall of the receptacle, and respective means located outside the receptacle and connected to the gas inlet means for supplying hydrogen having a purity of at least 99.9 percent at a pressure less than atmospheric pressure to the receptacle.

Other features which are considered as characteristic for the invention are set forth in the appended claims.

Although the invention is illustrated and described herein as method and device for crucible-free floating zone melting a crystalline rod, especially of semiconductor material, it is nevertheless not intended to be limited to the details shown, since various modifications may be made in the method and structural changes in the device without departing from the spirit of the invention and within the scope and range of equivalents of the claims.

The construction of the device of the invention and method of operation thereof, however, together with additional objects and advantages thereof will be best understood from the following description when read in connection with the accompanying single FIGURE of the drawing, wherein there is shown partly schematically and partly in section the device for crucible-free floating zone melting of a crystalline rod in accordance with my invention.

Referring now to the drawing, there is illustrated therein a receptacle 1 having a top and bottom formed with an opening, respectively, in which a sealing ring 2, 3 such as an oil seal, for example, is inserted so as to ensure a vacuum tight passage into the receptacle for drive shafts 4 and 5 on which a crystalline rod 6 is supported. The ends of the crystalline rod 6, consisting particularly of semiconductor material such as silicon, for example, are mounted respectively in rod end holders 7 and 8 of conventional construction that are located at the ends of the drive shafts 4 and 5 respectively. The drive shafts 4 and 5 and the respective holders 7 and 8 thereof are displaceable in the axial direction of the rod 6 as represented by the associated double-head arrows, and are rotatable about their common axis as represented by the associated curved arrows. An induction heating coil 10 extending through a vacuum-tightly sealed opening in a lateral wall of the receptacle 1, is preferably provided with a single turn surrounding the rod 6. Upon suitable electrical energization of the heating coil 10, a melting zone 9 is formed in the rod 6. As shown in the FIGURE, the induction heating coil 10 is stationary. Of course, the heating coil 10 can be made movable in the axial direction of the rod 6, while the drive shafts 4 and 5 are held

stationary against axial movement, or both the heating coil 10 and the drive shafts 4 and 5 can be movable in the axial direction of the rod 6. A holder 11 for the induction heating coil 10 can serve both for carrying electric current to the heating coil 10 as well as to supply coolant such as water thereto, when the heating coil is of the hollow tubular type known heretofore in the Art. A viewing window 12 is located in the lateral wall of the receptacle 1, located opposite the lateral wall thereof through which the heating coil 10 extends. A gas inlet is located near the bottom of one of the lateral walls, and a hydrogen gas supply tank 13 is connected by a tube system 14 through the gas inlet into the receptacle 1. The tube system 14 includes a reducing valve 15, a check or shut-off valve 16 as well as a total pressure gauge. Additive gas such as argon, helium, nitrogen with or without other gaseous substances mixed therewith, and the like, is contained in a tank 18 and is conducted through a tube system 19 into the tube system 14 from which it passes through the gas inlet into the receptacle 1. The tube system 19 includes a reducing valve 20, a reducing chamber 21 having a partial pressure gauge 22 connected thereto, and a check or shut-off valve 23. The hydrogen contained in the tank 13 is of extremely high purity. By diffusion through palladium and/or by freezing techniques, the hydrogen gas can be quite readily purified to a degree of purity of at least 99.9 percent. In fact, a purity of 99.999 percent is easily attainable. The necessity for having hydrogen of such a degree of purity is due to the fact that impurities such as oxygen, hydrocarbons, carbon monoxide or carbon dioxide have a deleterious effect on the growth of monocrystals.

The pressure of the atmosphere within the receptacle 1 is adjusted to a value between 30 and 600 Torr, preferably 150 Torr which, as aforementioned, minimizes contamination of the crystalline rod being processed. This adjustment of pressure is most easily effected by initially producing a high vacuum in the receptacle 1. Thereafter, a quantity of gaseous dopant additive, for example a mixture of phosphorus hydride or boron hydride and hydrogen or argon, predetermined for a specific resistance value, is admitted from the tank 18 through the tube system 19 and part of the tube system 14 into the receptacle 1. Subsequently, the quantity of hydrogen required for the desired total pressure, as indicated by the gauge 17, is conducted through the valves 15 and 16 of the tube system 14 into the receptacle 1.

In an example of the method of my invention, I provided a receptacle 1 having an inner volume of 250 liter, the crystalline rod 6 end supported in the receptacle 1 consisting of silicon. The reducing chamber 21 in my example had an inner volume of 10 liter. When the receptacle 1 was being evacuated, the shut-off valve 23 was kept open while the reducing valve 20 of the tube system 19 and the shut-off valve 16 and reducing valve 15 of the tube system 14 were kept closed, so that the reducing chamber 21 was also evacuated. After the evacuation was completed, the shut-off valve 23 was closed and the reducing valve 20 was opened so as to admit phosphorus hydride ( $\text{PH}_3$ ) into the reducing chamber 21 from the supply tank 18 containing a mixture of argon with 5 parts per million (ppm)  $\text{PH}_3$ , until the partial pressure gauge 22 registered a pressure of 120 Torr. The reducing valve 20 was then closed and the shut-off valve 23 was opened so that the contents of the reducing chamber flowed into the evacuated receptacle 1. After pressure equilibrium was attained, the shut-off valve 23 was again closed. Thereafter, the shut-off valve 16 and the reducing valve 15 were opened, and an amount of hydrogen from the supply tank 13 was admitted to the receptacle 1 until the total pressure gauge 17 registered 120 Torr. Then both the shut-off valve 16 and the reducing valve 15 were again closed.

The crystalline silicon rod 6 had an original specific resistance of 100  $\Omega\text{cm}$ . After the melting zone 9 was passed once through the rod 6 at a speed of 2 mm/min, the specific resistance of the rod 6 was then changed to 50  $\Omega\text{cm}$ .

If material of high resistivity, for example of 1000  $\Omega\text{cm}$  or the like, is to be produced, it is advantageous initially to carry

out one or more melting zones passes in high vacuum i.e., at a pressure below  $10^{-4}$  Torr, until the desired resistivity value is attained. Thereafter, the semiconductor rod 6 is then zone-melted one or more times in a pure hydrogen atmosphere without any dopant additive. Due to the highly pure hydrogen atmosphere, maintained for example at 150 Torr pressure, virtually no precipitation of impurities is permitted, so that the adjusted resistivity value of the rod 6 is maintained.

An annular coil having a single winding has been found to be particularly suitable as the heating source for the method and device of my invention. The voltage drop for such a coil is relatively low while the current density therefor is relatively high.

It is advantageous that, due to the pressure of the hydrogen gas, which is reduced relative to atmospheric pressure, the required coil energizing power is relatively small in spite of the very good heat conductivity of hydrogen. Thus, at a gas pressure of 150 Torr within the receptacle 6, only about double the energy is required as for carrying out the zone melting operation in high vacuum.

Following are two examples of gas mixtures wherein additive protective gas has been intermixed with hydrogen:

#### EXAMPLE 1

Hydrogen having a partial pressure of 30 Torr,  
Argon having a partial pressure of 70 Torr.

#### EXAMPLE 2

Hydrogen having a partial pressure of 20 Torr,  
Argon having a partial pressure of 60 Torr,  
Nitrogen having a partial pressure of 20 Torr.

The method of my invention can be combined to special advantage with various steps of the method disclosed in German Pat. Nos. 1 128 413 and 1 218 404 respectively relating to method for producing dislocation-free monocrystalline silicon by crucible-free zone melting (with bottle-neck shaped narrow portion) and method for crucible-free zone melting a crystalline rod, particularly a semiconductor rod (with lateral displacement of the resolidifying rod portion).

I claim:

1. In a method of floating zone melting a crystalline rod disposed in a sealed receptacle wherein an induction heating device surrounds the rod and forms a molten zone therein, the rod and heating device being relatively movable so as to pass the molten zone through the rod, the improvement which comprises evacuating the receptacle, and introducing a quantity of hydrogen gas of at least 99.9 percent purity into the evacuated receptacle so as to form a protective atmosphere therein having a pressure between 30 and 600 Torr, and maintaining the atmosphere at that pressure as the molten zone is passed through the rod.

2. Method according to claim 1 wherein the hydrogen gas has a purity of 99.995 percent.

3. Method according to claim 1 wherein the pressure of the atmosphere in the receptacle is about 100 Torr.

4. Method according to claim 1 wherein a gaseous dopant selected from the group consisting of phosphine and boron hydride is mixed with the hydrogen gas.

5. Method according to claim 1 which comprises passing a molten zone through the crystalline rod at least once in vacuo prior to zone melting the same in the hydrogen gas atmosphere.

6. Method according to claim 1 which comprises adding a further protective gas to the hydrogen gas.

7. Method according to claim 6 wherein the further protective gas is a noble gas.

8. Method according to claim 6 wherein the further protective gas is a gas selected from the group consisting of argon, helium and nitrogen.

9. Method according to claim 6 wherein the further protective gas is nitrogen having a partial pressure of at most 100 Torr.

10. Method according to claim 1 which comprises adding at least one further protective gas to the hydrogen gas in a quantity so that the total pressure of gas in the receptacle is between 30 and 600 Torr.

\* \* \* \* \*

5  
10  
15  
20  
25  
30  
35  
40  
45  
50  
55  
60  
65  
70  
75