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PROCESS FOR MAKING MONOCRYSTALLINE SILICON

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FIG. 1

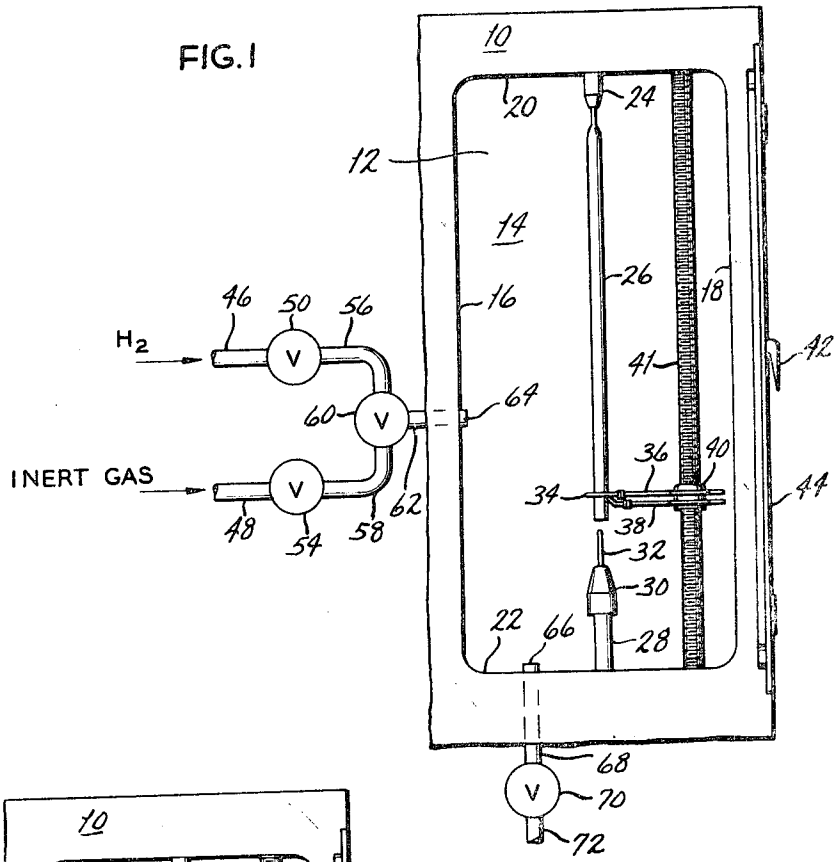
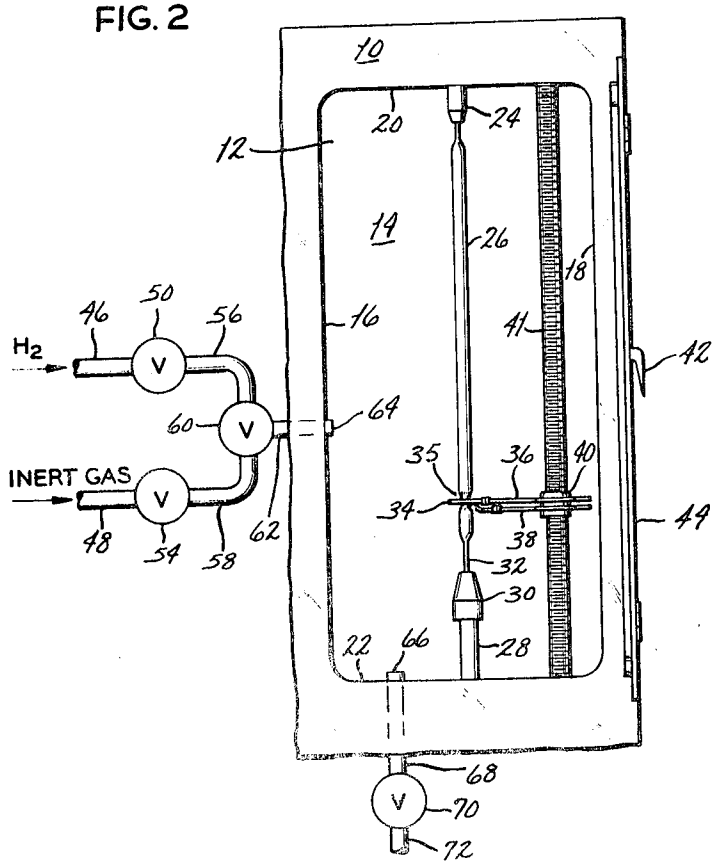


FIG. 2



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PROCESS FOR MAKING MONOCRYSTALLINE SILICON

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ABSTRACT OF THE DISCLOSURE

Disclosed is a process for making monocrystalline silicon in a zone refining operation. In this process, a gaseous mixture comprising predetermined volume percentages of hydrogen gas and a selected inert gas, such as argon, is introduced or "purged" into a chamber of a zone refiner both prior to and during a silicon zone refining operation. The presence of a selected volume percentage of no more than 5% hydrogen gas in this gaseous mixture which is purged into the zone refining chamber has been found to eliminate swirls in the silicon which had previously been discovered after etching zone refined silicon wafers processed in a zone refining operation using no hydrogen gas.

FIELD OF THE INVENTION

This invention relates generally to a float zone process for forming monocrystalline silicon and more particularly to the production of such silicon which is relatively free of swirls.

BACKGROUND OF THE INVENTION

The float zone or zone melting process for fabricating monocrystalline silicon has been well known for several years. In this process or variations thereof, a molten zone is initially produced at a selected location on a silicon rod by inductive radio frequency (RF) heating. Frequently, auxiliary heating means, such as a conductive heating plate, is utilized initially in combination with the RF inductive heating to rapidly heat up the silicon rod and reduce the zone refining start-up time. Thereafter, the molten zone is moved along the silicon rod by the production of relative motion between the silicon rod and an adjacent RF induction heating coil. Such relative motion may be provided by well known mechanical means, such as motor driven shafts, and the traverse rate of the molten zone along the silicon rod will depend upon the size of the molten zone employed and upon the power of the RF field produced by the adjacent induction heating coil. In the selection of the above parameters to determine this traverse rate, care must be taken to prevent zone fallout as will be appreciated by those skilled in the art.

DESCRIPTION OF THE PRIOR ART

Hitherto, it has been a standard procedure in the zone refining of elemental silicon to either: (1) carry out the zone refining operation in a vacuum which has been pulled on the chamber surrounding the silicon rod, or (2) use an inert gas, such as argon, to displace the air or other gas in the zone refining chamber prior to beginning the zone refining operation. The reason that the above procedures are employed is that molten silicon adversely reacts with oxygen in the zone refining chamber, with the resultant zone refined silicon rod having an undesirably high oxygen content therein.

The maintenance of a high vacuum condition within a zone refining chamber has several attendant disadvantages, among which include the requirement for bulky and expensive vacuum equipment which must be employed with each zone refiner. Additionally, vacuum systems can never completely remove all oxygen from the zone refining chamber. For these reasons, inert gases, such as argon, have frequently been used to replace vacuum systems and thus enable the zone refining operation to be carried out in an inert gaseous atmosphere which is relatively free of oxygen.

Monocrystalline silicon wafers which have been made utilizing the above inert gas zone refining prior art method have exhibited swirls which consist of clusters of imperfections that appear as shallow annular pits or hillocks on the etched planar surface of the wafer. The swirls were discovered, for example, after some of the wafers had been etched with a selected sirtl etchant which is described below in detail. These swirls tend to lower the minority carrier lifetimes in the monocrystalline silicon and further act as preferential diffusion paths for impurities during the zone refining operation.

SUMMARY OF THE INVENTION

The general purpose of this invention is to provide new and improved high quality swirl-free monocrystalline silicon and a zone refining process for making same. The present inventive process includes all of the advantages of present state-of-the-art processes for producing monocrystalline silicon, and yet produces a monocrystalline silicon which is free of these previously discovered swirls on the etched surface of the silicon wafers. To attain this, a chosen amount of hydrogen gas is introduced or "purged" into the zone refining chamber along with an inert gas both in preparation for and during a zone refining operation. It has been observed that by so purging the zone refining chamber with a controlled mixture of a hydrogen gas and a selected inert gas, the swirls in the monocrystalline silicon can be eliminated.

Accordingly, an object of the present invention is to provide an improved zone refined monocrystalline silicon which is free of swirls.

Another object of this invention is to provide a new and improved zone refining process for the production of monocrystalline silicon. The swirl-free monocrystalline silicon produced by the present process exhibits a desirable high minority carrier lifetime characteristic.

These and other objects and features of this invention will become more fully apparent in the following description of the accompanying drawing.

DRAWING

FIG. 1 is a perspective view of a silicon zone refining chamber and associated purge gas flow lines which may be utilized in performing the process according to the present invention. The zone refining apparatus shown in FIG. 1 is in its pre-startup condition.

FIG. 2 shows the same zone refining apparatus illustrated in FIG. 1 and in operation during a zone refining pass in which the present inventive process is carried out.

THE INVENTION

Referring to FIGS. 1 and 2 of the drawing, the reference numeral **10** represents a support panel for a zone refining chamber, generally designated by the reference numeral **12**. The chamber **12** comprises a back wall **14**, sidewalls **16** and **18**, a top wall **20** and a bottom wall **22**. In FIGS. 1 and 2, the front wall of the chamber **12** opposite the back wall **14** has been omitted so that the zone refining apparatus in the chamber **12** can be seen and described.

An elongated polycrystalline silicon rod **26** is secured to the top wall **20** of the chamber **12** by a rod holder **24** which can be of conventional construction. The rod holder **24** is designed to hold the silicon rod **26** such that it extends substantially in the vertical direction in the chamber

12. While the position of the silicon rod **26** can deviate from a strictly vertical position, any substantial deviation is generally undesirable since it promotes the falling out of the molten zone of silicon and may necessitate the use of levitation means to prevent the loss of the molten zone.

Beneath the lower end of the polycrystalline silicon rod **26** is a monocrystalline silicon seed crystal **32** which is held in the vertical position shown by a seed holder chuck **30**. The seed holder chuck **30** is supported atop a rotatable shaft **28** which extends through the bottom wall **22** of the zone refining chamber **12**. The rotatable shaft **28** is longitudinally movable so that the silicon seed crystal **32** can be fused to the lower end of the silicon rod **26** as shown in FIG. 2 during the initial phase of the zone refining operation.

Surrounding the silicon rod **26** is an RF heater coil **34** joined to conductive arms **36** and **38** which are securely attached to a transverse member **40** on the traverse rod **41**. The traverse rod **41** may be driven by any suitable means (not shown) to rotate the rod **41** and thus move the transverse member **40** up the silicon rod **26** during the zone refining operation. However, it should be understood that the present invention is not limited to this type of "uprefining," nor is it limited to any mechanical means for producing the relative movement between the RF work coil **34** and the silicon rod **26**.

The above-described zone refining apparatus within the chamber **12** is accessible to an operator via a front panel **44** having a door handle **42** thereon as shown. For a more detailed discussion of the type of the zone refining apparatus shown in the drawing, reference may be made to U.S. Pat. 3,251,658, issued to A. Hambach et al. on May 17, 1966 and assigned to the present assignee.

A pair of gas flow lines **46** and **48** are connectable to the indicated sources (not shown) of hydrogen gas and a selected inert gas, respectively. The hydrogen gas, H_2, and the inert gas are controlled by gas flow valves **50** and **54** in a manner to be described hereinafter, and the regulated hydrogen and inert gases are passed through gas lines **56** and **58** to a common flow control valve **60** which regulates the total volume of the H_2-inert gas mixture entering the zone refining chamber **12** via gas line **62** and opening **64**. The total gaseous mixture introduced or purged via opening **64** may be controlled in accordance with the opening or setting of the valve **62** and is also dependent upon the gas pressures within the individual gas lines **46** and **48**. An exit gas line **68** having an opening **66** therein extends to the outside of the zone refining chamber **12**, and the gaseous mixture exiting the chamber **12** is controlled by another suitable flow control valve **70**. The flow or purge control of inert gases introduced into a silicon zone refining operation is well known in the semiconductor art and is therefore not described in detail herein.

ZONE REFINING STARTUP AND OPERATION

Prior to beginning the first zone refining pass, and with the zone refining apparatus in the position shown in FIG. 1, a mixture of hydrogen gas, H_2, and a selected inert gas is passed through the flow control valve **60** and into the zone refining chamber **12** to displace the air or other gases in the chamber **12**. This gaseous mixture enters the chamber **12** via line **62** and exits the chamber **12** via line **68** at a continuous purge or flow rate. This gas purging of the chamber **12** is allowed to continue for approximately 20 minutes prior to beginning the zone refining operation to be further described.

A preferred range by volume percentages of hydrogen gas to the total gaseous mixture entering the chamber **12** is from between approximately 0.1 and 5.0%, and a corresponding preferred range of the selected inert gas entering the chamber **12** is from between approximately 99.9% and 95%, respectively. Within this preferred range, a gaseous mixture of approximately 1% H_2 and 99% inert argon gas has been used commercially to eliminate all swirls in the zone refined silicon. These gas volume percentages have been successfully used continuously during both pre-startup gas purging and the continuous dynamic purging of the zone refining chamber during a zone refining operation. However, by appropriately controlling the flow control valves **50** and **54**, these volume percentages may be varied within the above range to produce swirl-free monocrystalline silicon within the scope of the present invention.

It has been observed that when more than approximately 2% H_2 in the gaseous purging mixture is used, a subsequent undesirable preferential etching of the zone refined silicon will occur when the zone refined silicon water are etched in CP_4. This etchant is a mixture of acetic acid, nitric acid and hydrofluoric acid which is sold commercially under the trade name CP_4. The latter etching step is utilized prior to the sirtl etch step referred to above, and the acid etchant CP_4 is applied to wafers obtained from the zone refined monocrystalline silicon rods to remove the saw damage therefrom. When slightly more than 2% H_2 gas is used in the purging mixture entering the chamber **12**, the etchant CP_4 has been found to preferentially etch the monocrystalline silicon wafers and thereby leave dished-out areas on the etched wafer surface. This latter undesirable preferential etching has been found to occur only on wafers that were sliced very near the seed end of the monocrystalline silicon rod. If the percentage of H_2 gas in the gaseous purging mixture is increased to approximately 5%, this undesirable preferential etching of the silicon wafers by CP_4 becomes noticeably increased and substantially reduces wafer processing yields.

The inert gas entering line **48** may be selected from the group of inert gases consisting of helium, argon and krypton. This inert gas is purged in a gaseous mixture with the hydrogen gas in the above-described percentages via the gas line **62** into the zone refining chamber **12**, both prior to and during the zone refining operation. Advantageously, the pressure within the zone refining chamber **12** is maintained between 0.8 and 2.0 atmospheres, and this pressure may be regulated in accordance with the pressures of the sources of hydrogen and inert gas and the valve settings of the gas intake flow control valves **50**, **54** and **60** and the exit flow control valve **70**.

After the zone refining chamber **12** of FIG. 1 has been purged with the above mixture of hydrogen and a selected inert gas for approximately 20 minutes, the silicon zone refining operation is continued by fusing the monocrystalline seed crystal **32** to the bottom of the polycrystalline silicon rod **26** at a selected elevated zone refining temperature. This temperature is typically in the vicinity of 1420° C. Once the seed crystal **32** is fused to the silicon rod **26**, a liquid molten zone will begin to form on the bottom of the silicon rod **26**, and this zone may be moved or "passed up" the silicon rod **26** as the RF induction heating coil **34** is moved vertically up the traverse rod **41**. This liquid molten zone **35** is shown in FIG. 2 and is slightly smaller in diameter than the diameter of the polycrystalline silicon rod **26**. As the molten zone **35** moves up the silicon rod **26**, the upper interface between the zone **35** and the rod **26** is continuously melting whereas the lower interface between the zone **35** and the silicon rod **26** resolidifies. The molten zone **35** may be moved along the silicon rod **26** one or more times, if desired, and each of these movements is referred to as a single "pass."

The gaseous mixture of hydrogen and an inert gas is purged into the chamber **12** throughout the complete zone refining operation. Using 1.0% H_2 gas and 99.0% argon in the purging mixture, the H_2-argon mixture continuously purged into the opening **64** in the gas line **62** during a zone refining operation. By purging the zone refining chamber **12** with the above H_2-argon gaseous mixture, monocrystalline silicon rods with orientations in the 111, 100 and 110 planes have been formed from polycrystalline rods and have ranged in resistivity from 0.1 ohm centimeter to intrinsic. Both P and N type swirl-free mono-

crystalline silicon rods have been made using the above-described process.

Wafers sliced from these monocrystalline silicon rods and previously etched with CP_4 as noted above, are further etched in a selected sirtl etchant. This sirtl etchant is used to expose so-called dislocations on the wafer surface and will also expose the swirls on the wafer surface if any exist. Wafers which were fabricated using the above-described gas purging process according to the present invention and then etched with a selected sirtl etchant were found to be completely free of any swirls on the etched planar surface thereof. The particular sirtl etchant used was a solution of distilled water, chromium trioxide (CrO_3) and hydrofluorine acid (HR). In preparing this solution, 100 grams of 99.9% CrO_3 and 100 grams of 48–51% HF were added to 200 milliliters of distilled water.

The invention described above is not limited to the particular zone refining apparatus shown in FIGS. 1 and 2, and any other suitable zone refining apparatus and appropriate gas flow control apparatus equivalent to that shown in the drawing may be utilized within the scope of this invention.

I claim:

1. A process for fabricating swirl-free monocrystalline silicon in a chamber of a zone refiner which includes introducing predetermined volume percentages of hydrogen gas from approximately between 0.1% and 5% by volume and a selected inert gas from between approximately 99.9% and 95% by volume, respectively, into said chamber to displace existing gases therein during a zone refining operation and thereby eliminate swirls from silicon prepared in said zone refiner.

2. The process defined in claim **1** wherein said hydrogen gas is introduced into said chamber at approximately 1.0% by volume and said selected inert gas is introduced into said chamber at approximately 99.0% by volume.

3. The process defined in claim **1** wherein said inert gas is selected from the group of inert gases consisting of argon, helium and krypton.

4. The process defined in claim **3** wherein said hydrogen gas is introduced into said chamber at approximately 1.0% by volume and said select inert gas is introduced into said chamber at approximately 99.0% by volume.

5. A process for fabricating swirl-free monocrystalline silicon in a zone refining operation which includes the steps of:

(a) displacing the air within a zone refining chamber by purging said chamber with a mixture of hydrogen gas from approximately between 0.1% and 5% by volume and a selected inert gas from approximately between 99.9% and 95% by volume, respectively, for a predetermined time prior to beginning a zone refining operation, and

(b) making a zone refining pass on a polycrystalline silicon rod to convert said rod to monocrystalline silicon while simultaneously purging said zone refining chamber with the above said mixture of hydrogen gas and a selected inert gas at a predetermined flow rate through said chamber during said zone refining operation.

6. The process defined in claim **5** wherein said mixture of hydrogen gas and said selected inert gas is purged into said zone refining chamber for a time interval prior to starting the zone refining operation sufficient to displace substantially all existing gases within said chamber and thereby reduce the oxygen content therein prior to initiating a zone refining operation.

7. The process defined in claim **6** wherein said hydrogen gas is introduced into said chamber at approximately 1.0% by volume and said selected inert gas is introduced into said chamber at approximately 99.0% by volume.

8. The process defined in claim **6** wherein said selected inert gas is selected from the group of gases consisting of argon, helium and krypton.

9. The process defined in claim **7** wherein said inert gas is selected from the group of gases consisting of argon, helium and krypton.

10. In a process for fabricating monocrystalline silicon in a zone refiner which includes purging a chamber of the zone refiner with a gaseous mixture including an inert gas to displace oxygen within the chamber both prior to and during a silicon zone refining operation, the improvement comprising: introducing a selected volume percentage of hydrogen gas from between approximately 1.0% and 2.0% by volume into said purging mixture to eliminate any swirls in the monocrystalline silicon prepared in the zone refiner.

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U.S. Cl. X.R.

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