Device and Method for Producing a Single Crystal, Single Crystal and Semiconductor Wafer

The invention relates to a device for producing a single crystal of semiconductor material, which is contaminated only slightly by iron. The invention also relates to a method for producing such a single crystal. The invention furthermore relates to a single crystal of semiconductor material produced by the method and to a semiconductor wafer cut from the single crystal.

A suitable device comprises a chamber in which there is a crucible, which is embedded in a support crucible made of material containing carbon, a heater for heating the crucible and thermal insulation, which is arranged between the heater and the crucible in order to protect the chamber. A radiation shield which encloses the growing crystal and serves to control the cooling rate of the single crystal, and to deflect an inert gas with which the device is flushed during production of the single crystal, is also customary.

According to JP-2000327485 A, it is possible to produce single crystals of silicon in which the iron concentration is less than $2*10^9$ atoms/cm^3. In order to produce such single crystals, it is necessary to purify the polycrystalline intermediate product in an elaborate process. Said concentration, however, is still not a sufficient feature for a single crystal which is contaminated only slightly with iron in the context of the invention. Rather, what is crucial is that there is also a low iron concentration in the edge region of the single crystal. As Barraclough, K.G. and Ward, P.J.(Proc. Electrochem. Soc., 83-9, 388-395 (1983)) have observed, iron reaches the edge of the single crystal via a mechanism which is based on gas phase transport, diffuses from there into the single crystal and significantly increases the iron concentration in the edge region of the single crystal. In order to counteract this, it has been proposed in the document inter alia to replace a

holder consisting of stainless steel for the seed crystal by a holder made of molybdenum.

According to WO 02/057518 A2, it is possible to produce single crystals of silicon in which the iron concentration in an edge region is less than 0.8 ppta ($3.99*10^{10}$ atoms/cm^3). In order to achieve this result, all components of the device that consist of material containing carbon must contain this material in a particularly low-iron form, and this material must be encapsulated by a likewise particularly low-iron layer of silicon carbide.

In WO 01/81661 A1, it is proposed to use a coated tube for directing the inert gas stream, in which case the coating should contain at most 0.5 ppm iron. According to the method described there, it is possible to produce monocrystalline semiconductor wafers of silicon in which the iron concentration is not more than $1*10^{10}$ atoms/cm^3.

It is an object of the present invention to provide an economical alternative by which it is possible to produce a single crystal of semiconductor material with an iron concentration which is not more than $1*10^{9}$ atoms/cm^3, and which is not exceeded even in the edge region of the single crystal and in the edge region of wafers cut from the single crystal.

The invention relates to a device for producing a single crystal of semiconductor material, comprising a chamber and a crucible which is arranged in the chamber and is enclosed by a crucible heater, a radiation shield for shielding a growing single crystal and thermal insulation between the crucible heater and an inner wall of the chamber, which device comprises a resilient seal which seals a gap between the inner wall and the thermal insulation and forms an obstacle for the transport of gaseous iron carbonyls to the single crystal.

The invention also relates to a method for producing a single crystal of semiconductor material by pulling the single crystal

from a crucible, which is arranged in a chamber and is enclosed by a crucible heater, wherein a gap between thermal insulation and an inner wall of the chamber is sealed with a resilient seal, which forms an obstacle for the transport of gaseous iron carbonyls to the single crystal.

The invention furthermore relates to a single crystal of semiconductor material produced according to said method, comprising a section of cylindrical shape which has a circumference, a radius R and an edge region, which extends from the circumference to a distance of up to R-5 mm radially into the single crystal and has an iron concentration, wherein the iron concentration in the edge region is less than $1*10^9$ atoms/cm^3.

The invention lastly relates to a semiconductor wafer cut from the single crystal having a circumference, a radius R and an edge region, which extends from the circumference to a distance of up to R-5 mm radially into the semiconductor wafer and has an iron concentration, wherein the iron concentration in the edge region is less than $1*10^9$ atoms/cm^3.

The semiconductor material is preferably silicon, optionally in combination with germanium and/or opto-, magnetoelectronic semiconductor compounds. The invention can be used irrespective of the diameter of the single crystal produced, or of the semiconductor wafer produced. Nevertheless, diameters of 150 mm, 200 mm and 300 mm or more are particularly preferred.

The inventors have identified a main source of the contamination of the single crystal with iron as being the chamber, which is usually formed by a cooled container whose walls consist of an alloy containing iron, particularly stainless steel. It is suspected that carbon monoxide which is formed owing to the heating of carbon-containing components of the chamber, particularly the support crucible and the thermal insulation, reaches the inner wall of the chamber via the inert gas stream and by diffusion. At the inner wall which is still

at a temperature of more than 100°C, volatile iron carbonyles are formed which can enter the gap between the thermal insulation and the inner wall of the chamber and reach the growing single crystal. Upon contact with the single crystal which is at a temperature of several hundred degrees Celsius, the iron carbonyles decompose into elementary iron and carbon monoxide in reverse of the reaction by which they are formed. At the prevailing temperatures, the iron diffuses into the peripheral regions of the single crystal where it increases the iron concentration. By this mechanism, iron is also distributed over components of the device which are hot enough to cause decomposition of the iron carbonyles. These include for example the support crucible, the thermal insulation for protecting the chamber and the radiation shield.

Those measures which have previously been proposed for reducing the contamination of the single crystal by iron do not take the chamber wall into account as a contamination source, and they do not provide an economically satisfactory solution to the problem.

According to the present invention, the gap between the thermal insulation and the wall of the chamber is closed by a resilient seal at least at one position, so that gaseous iron carbonyles must overcome this obstacle in order to be able to travel up along the inner wall of the chamber and subsequently reach the single crystal. Owing to manufacturing tolerances, the gap between the thermal insulation and the inner wall of the chamber exists even when the thermal insulation is made with a tight fit. It is, however, more customary to provide the gap deliberately in order to allow thermal expansion of the thermal insulation and the means for fastening it the necessary space for this expansion movement.

The seal to be provided according to the invention is resiliently deformable and fitted into the gap so that the gap remains closed even in view of thermal expansion. The seal may extend over the entire gap, i.e. completely fill the gap. If

only for economic reasons, however, it is preferable to save on sealing material so that the gap is left remaining at least partially. It is particularly preferable to form the seal as a ring which preferably extends over an axial width of from 50 to 200 mm, particularly preferably about 100 mm, in which case a plurality of such rings may also be arranged above one another. In principle, however, it is sufficient for the seal to form an obstacle extending transversely to the axis of the single crystal, which limits the transport of gaseous iron carbonyles along the inner wall of the chamber to the single crystal. The transport is regarded as having been limited when the iron concentration in the edge region of a single crystal, which has been produced by using the seal, is at least 50% lower than in a single crystal which was pulled under otherwise equal conditions but whose production did not employ the seal. Instead of the iron concentration in the edge region of the single crystal, it is also possible to refer to the concentration in the edge region of a semiconductor wafer cut from the single crystal. The edge region is a region which extends radially inwards over a distance of preferably up to 5 mm from the circumference of the single crystal, or a semiconductor wafer cut therefrom. The iron concentration is preferably measured at a position which lies at a radial distance of 1, 2, 3, 4 or 5 mm from the circumference.

The seal consists of a resilient material, preferably graphite felt, which contains carbonized or graphitized carbon fibers. The material is preferably resilient enough to be wound in one layer around a test rod with a diameter of from 50 to 80 mm without breaking, with a winding direction transverse to or along the material web. The breaking strain of the material according to DIN 52143 is preferably from 2 to 5% along and from 13 to 20% transversely to the material web. The gas permeability of the material according to DIN 53887 is preferably from 25 to 50 $cm^3/(cm^2*s)$, with a pressure difference of 300 Pa in nitrogen. The iron content of the material according to DIN ISO 8658 is preferably less than 0.3 mg/kg. Graphite felt of the brand Sigratherm® GFA 10 from the

manufacturer SGL Carbon is particularly preferred. This material is available in the form of webs with a thickness of 9-10 mm. In multiple layers or in a folded state to form a labyrinth seal, it is even suitable for sealing a gap between the inner wall of the chamber and the thermal insulation which is thicker than the thickness of a web.

An additional measure which is proposed in order to achieve the aforementioned object consists in providing the inner wall of the chamber with a ceramic coating. A coating of aluminum oxide is particularly preferred. The coating prevents direct contact of carbon monoxide and the inner wall of the chamber, and thus reduces the formation of iron carbonyles.

A further measure, which may be taken in combination with the resilient seal and the ceramic coating or only in combination with the resilient seal, consists in providing an active cooling system for cooling the single crystal. The term active cooling system is intended to mean cooling components which extract heat by using supplied energy, for example components which operate according to the heat exchanger principle. Active cooling systems are also used to control the defect formation in silicon crystals, for example, and may be part of the conventionally provided radiation shield which encloses the growing single crystal. Their contribution to achieving the object of this invention consists in providing temperatures on the surface of the growing single crystal, and in its environment, at which iron carbonyles can no longer thermally decompose. An example of a suitable active cooling system, which is integrated into a radiation shield, is described in US-5,567,399.

As a further additional measure, it is lastly proposed that the thermal insulation and all other components made of material containing carbon, which are located in the chamber and are heated to temperatures of more than 200°C during the production of the single crystal, be replaced at regular intervals. These

components may optionally be reused, after deposited iron has been cleaned from their surfaces.

A preferred embodiment of the invention will be explained in more detail below with reference to a figure. The figure schematically shows a device for producing a single crystal of semiconductor material according to the Czochralski method, the representation being limited to showing those features which contribute to understanding of the invention. Bold, solid arrows symbolize the primary direction of an inert gas stream conventionally used for flushing the chamber. Broken arrows symbolize the path by which iron carbonyles can reach the single crystal, if they are not prevented from doing so according to the present invention. The device comprises a chamber 1 in which a crucible 2 and further components, which fulfill functions during the production of a single crystal 3, are fitted. These components include a mechanism 4 for pulling the single crystal 3 from a melt 5 which is contained in the crucible 2, a support crucible 7 arranged on a shaft 6 in order to hold the crucible 2, and a crucible heater 8 enclosing the crucible. The inner wall 9 of the chamber is protected by thermal insulation 10 against the heat given off by the crucible heater 8. Thermal insulation is conventionally also provided in the form of further components at other positions, for example insulation in the region of the shaft 6 and the bottom region of the chamber. Between the thermal insulation 10 and the inner wall 9 of the chamber, there is a gap 11 which is closed by a resilient seal 12. According to a preferred embodiment, the seal 12 is designed as a ring. The growing single crystal 3 is enclosed by a radiation shield 13 which may itself comprise a thermally insulating elements, and which is fastened on a support 16. According to another preferred embodiment of the invention, there is an active cooling system 14 for cooling the single crystal in addition to the radiation shield or integrated into it. According to another preferred embodiment of the invention, the inner wall 9 of the chamber is also provided with a ceramic coating 15, which prevents carbon monoxide and iron from the wall material reacting to form iron

carbonyles. The coating 15 is represented only indicatively in the figure.

Example:

In a device for pulling single crystals having the features of the installation outlined in Fig. 1, without a coating 15 of the inner wall 9 but in particular with a resilient seal 12 designed as a ring with an axial width of about 100 mm, rod-shaped single crystals of silicon with a diameter of 200 mm were pulled and the iron concentration was determined in the edge region of wafers, which were cut from the single crystals. The wafers measured were taken from the same axial rod position. Type A wafers came from single crystals which were produced with the device, the resilient seal according to the invention not having been used. The single crystals which gave type B wafers were produced in the same device, but with the difference that the gap between the inner wall of the chamber and the thermal insulation was sealed by the ring of Sigratherm® GFA 10 type graphite felt extending transversely to the axis of the single crystal. An active cooling system, which was integrated into the radiation shield, was used in addition to the resilient seal in order to produce the single crystals which gave type C wafers. The results of the iron concentration determinations at three positions with radial distances of 1 mm, 3 mm and 5 mm from the edge R of the wafers are collated in the following table. The iron concentration outside the edge region was in no case higher than in the edge region. The concentrations were determined according to ASTM F 391.

Table:

Type	Position R-1 mm Fe [atoms/cm^3]	Position R-3 mm Fe [atoms/cm^3]	Position R-5 mm Fe [atoms/cm^3]
A	$3*10^{10}$	$2.3*10^{10}$	$1.3*10^{10}$
B	$1.5*10^{10}$	$1*10^{10}$	$0.6*10^{10}$
C	< LoD	< LoD	< LoD

The results show that the iron concentration could be reduced by at least 50% by providing the seal. The iron concentration at the positions studied in type C wafers actually lay below the limit of detection (LoD), which is $1*10^9$ atoms/cm^3.

Patent Claims:

1. A device for producing a single crystal of semiconductor material, comprising a chamber and a crucible which is arranged in the chamber and is enclosed by a crucible heater, a radiation shield for shielding a growing single crystal and thermal insulation between the crucible heater and an inner wall of the chamber, which device comprises a resilient seal which seals a gap between the inner wall and the thermal insulation and forms an obstacle for the transport of gaseous iron carbonyls to the single crystal.

2. The device as claimed in claim 1, wherein the seal reduces the transport of iron carbonyls to the single crystal by at least 50%.

3. The device as claimed in claim 1 or claim 2, wherein the resilient seal is designed as a ring.

4. The device as claimed in one of claims 1 to 3, wherein the resilient seal consists of graphite felt which contains carbonized or graphitized carbon fibers.

5. The device as claimed in one of claims 1 to 4, which device comprises an active cooling system for cooling the growing single crystal.

6. The device as claimed in one of claims 1 to 5, which device comprises a ceramic coating with which the inner wall is coated.

7. A method for producing a single crystal of semiconductor material by pulling the single crystal from a crucible, which is arranged in a chamber and is enclosed by a crucible heater, wherein a gap between thermal insulation and an inner wall of the chamber is sealed with a resilient seal, which forms an obstacle for the transport of gaseous iron carbonyls to the single crystal.

8. The method as claimed in claim 7, wherein the transport of iron carbonyls to the single crystal is reduced by at least 50%.

9. The method as claimed in claim 7 or claim 8, wherein the single crystal is actively cooled.

10. The method as claimed in one of claims 7 to 9, wherein the inner wall of the chamber is coated with a ceramic coating.

11. The method as claimed in one of claims 7 to 10, wherein deposited iron is cleaned at regular intervals from the surface of carbon-containing components of the chamber.

12. A single crystal of semiconductor material, comprising a section of cylindrical shape which has a circumference, a radius R and an edge region, which extends from the circumference to a distance of up to R-5 mm radially into the single crystal and has an iron concentration, wherein the iron concentration is less than $1*10^9$ atoms/cm^3.

13. A semiconductor wafer having a circumference, a radius R and an edge region, which extends from the circumference to a distance of up to R-5 mm radially into the semiconductor wafer and has an iron concentration, wherein the iron concentration in the edge region is less than $1*10^9$ atoms/cm^3.