

Method For The Crystal Pulling Of A Doped Monocrystalline Crystal From Silicon

The invention relates to a method of pulling a doped single crystal of silicon.

The growing of crystals is an important prerequisite for the production of semiconductor components. Semiconductor crystal growing methods have been improved in order to obtain monocrystalline semiconductor blocks that may have, for example, a diameter of 200 mm to 300 mm and a length of more than two meters.

Components for the control of large currents (power components) require highly doped silicon crystals that are processed further to give the corresponding components.

One of the challenges in the growing of highly doped silicon by the Czochralski method is to increase the maximum dopant concentration or to reduce the minimum resistivity without reducing the yield of utilizable crystals.

Prior art

DE 10 2019 210 254 A1 describes a method of pulling a single crystal of silicon having a specific resistivity of not more than 20×10^{-3} ohm cm, wherein the first phase of the crystal growing process is optimized with the aim of reducing the probability of occurrence of dislocations.

EP 3 864 197 A1 is concerned with a method of controlling the concentration of the dopant in the melt, with the aim of reducing the occurrence of dislocations.

DE 10 2021 206 550 A1 describes a method of pulling a single crystal with a very low resistivity using a magnetic field.

The phenomenon of constitutional supercooling is not a problem at first with a relatively low doping level which is generally used for the growing of semiconductor crystals.

However, during crystal growth from a highly doped melt - where the dopants have a small equilibrium segregation coefficient much smaller than one - constitutional supercooling may occur in the melt at the interface between melt and crystal. The effect of this is that the rod dislocates and is no longer usable for the component process.

A method of pulling crystals can be modified in a wide variety of ways in order to produce crystals with a moderate dopant level. For example, crystal rotation, crucible rotation, magnetic field position and strength, distances between different installed components, to name just a few.

If the dopant level is to be increased, i.e. the resistivity in the crystal is to be lowered further, it is found that many processes that can be established without difficulty with high resistivity are subject to dislocation, i.e. reject material.

What is common to the prior art citations given is that they do not show a directed method by which processes can be optimized to that effect. It is necessary to undertake many costly experiments in which it is not clear from the outset whether, firstly, the corresponding crystal meets the requirements and, secondly, the process proposed also provides suitable crystals with sufficient stability.

It is therefore an object of this invention to provide a method that makes it possible to modify crystal pulling processes such that they have a high dopant level and, at the same time, meet quality demands with simultaneously reduced experimental complexity.

This object is achieved by the methods described in the claims.

Brief description of the figures

Figure 1 shows the factor f_{CS} as a function of specific resistivity for the dopants phosphorus (P), arsenic (As) and antimony (Sb).

Figure 2 shows the sum total of the simulated parameter $\overline{CS}$ and an offset constant C_{Offset} for an example process **A**, shown as a function of resistivity (dotted curve).

The limiting resistivity at which the crystal is still just pullable is ascertained by varying the resistivity until the curve of the sum total of the simulated parameter $\overline{CS}$ at the triple point of the simulated crystal and the offset constant C_{Offset} becomes zero.

The dark-colored bar drawn in is intended to show the resistivity range where there is no prospect of successful crystal pulling. There is realistically a small transition region (lightly hatched) in which crystal pulling is possible at high risk, but is inadvisable for economic reasons.

Figure 3 shows the sum of the simulated parameters $\overline{CS}$ at the triple point of the respective crystal and an offset constant C_{Offset} for four example processes (**A** “dashed”, **B** “solid”, **C** “dash-dot”, **D** “dash-dot-dot”), each shown as a function of resistivity.

The respective limiting resistivities at which a crystal is still just pullable have been symbolized by the arrows directed downward on the abscissa axis.

Detailed description of the invention

As already mentioned, the phenomenon of constitutional supercooling is not problematic at first at a relatively low doping level which is generally used for the growing of semiconductor crystals. It is only the increase in the desired dopant concentration that can lead to constitutional supercooling and hence to a high probability of dislocations and hence to complete failure of the respective crystal.

The inventors have tried successfully, among other efforts, to use a considerably modified computer simulation method to confine and to solve the stated problem.

The physical effect of constitutional supercooling is described, for example, in the thesis by L. Stockmeier (ISBN 978-3-8396-1345-0, “Heavily n-type doped silicon and the dislocation formation during its growth by the Czochralski method”).

The underlying mathematical model for numerical modelling of this problem together with suitable software are described in the necessary details in Mukaiyama et al. [Y. Mukaiyama, V. Artemyev, K. Sueoka, J. Crystal Growth, 597 (2022) 126844, <https://doi.org/10.1016/j.jcrysgr.2022.126844>].

- 5 The inventors have recognized that major adaptations are needed to achieve significant improvements in yield. These major adaptations are elucidated hereinafter.

A value **CS** which is calculated at the interface between melt and crystal is defined here as:

$$CS = \frac{\partial T}{\partial n} - f_{CS} \frac{\partial c}{\partial n},$$

- 10 where $\frac{\partial T}{\partial n}$ represents the partial derivative of temperature and $\frac{\partial c}{\partial n}$ the partial derivative of the concentration of the dopant along the normal to the interface between crystal and melt in the melt.

- The factor f_{CS} is a function of specific resistivity and the material properties of the dopant and can be ascertained with the aid of the material data constants and the
15 “density/resistivity” diagram of the dopant (*SEMI* Standard *MF723-0307*, 2012 Practice for conversion between resistivity and dopant or carrier density for boron-doped, phosphorus-doped, and arsenic-doped silicon).

- Figure 1** shows this factor f_{CS} as a function of specific resistivity for different dopants such as phosphorus, arsenic or antimony. It is easily possible to determine this factor
20 for other dopants as well, and hence the inventive method is not limited to these dopants.

- The numerical differences in f_{CS} for different dopants are attributable to differences in the ionized fraction of the dopant and in the segregation coefficients. The material properties can explain the difference for phosphorus (P), arsenic (As) and Sb as
25 dopants.

There follows an elucidation of the modified boundary conditions for heat transfer and the transfer of dopants for the modeling.

For the 3D simulations conducted, the temperature at the interface between crystal and melt was assumed to be constant.

- 5 The inventors found that the boundary conditions for the concentration (segregation boundary conditions) from Mukaiyama et al. [Y. Mukaiyama, V. Artemyev, K. Sueoka, J. Crystal Growth, 597 (2022) 126844] are valid for a positive crystallization rate.

$$-\rho_{melt}D_{melt}\frac{\partial c}{\partial n} = \rho_{crys}V_{crys}c_{melt}(1 - k), \quad c_{crys} = kc_{melt}$$

- 10 The inventors also found that, in the case of a negative crystallization rate (= melting), this equation should preferably be replaced by the following equation:

$$-\rho_{melt}D_{melt}\frac{\partial c}{\partial n} = \rho_{crys}V_{crys}(c_{melt} - c_{crys})$$

In this equation, c is the concentration by mass, ρ_{melt} is the density of the melt, D_{melt} is the coefficient of diffusion of the dopant in the melt, c_{crys} is the concentration of the dopants in the crystal and n is the normal to the interface at the melt or growth front.

- 15 The parameter c_{crys} is a value known from current calculations when the crystallization rate is positive, and is a function of crystal length.

- In the present invention, the value thereof has been approximated by the average dopant concentration in the crystal. It has been found that the exact values of c_{crys} are not needed for the calculation. Moreover, it is difficult to implement them in the software.
- 20

An experimental form of the interface between melt and crystal can be ascertained by cutting out a piece of crystal to be examined, a rectangular sheet (called a plaque), by means of two longitudinal sections along the center of the piece of crystal. This plaque can then be examined with regard to variations in resistivity. The added dopant is

incorporated irregularly into the crystal. The dopant preferably contains boron or phosphorus. This leads to a locally inhomogeneous resistivity distribution of the silicon, called “striations”. Even though great efforts are taken to avoid striations in order not to suffer adverse effects in the component process, striations in the doped rod are nevertheless always measurable. Since the dopant is incorporated from the melt into the crystal along the melt/crystal interface, it is possible by means of the analysis of the measured resistivity distribution to ascertain the original shape of the interface between crystal and melt in the form of growth striations.

Unsteady 3D simulations are needed for the simulation, and there are two means of conducting them:

Either the shape of the interface between crystal and melt is adjusted by fitting of the Stefan boundary condition such that they correspond to reality, or the shape of the interface is fixed, accepting that the Stefan condition is not necessarily fulfilled.

Both approaches may be unsuitable for the calculations under particular conditions. In the first case, the interface may vary from the experimental interface, which affects the calculations of the flow and the species. In the second case, the calculated crystallization rate would be wrong, and accordingly also the distribution of the species at the interface, since it follows the segregation boundary conditions.

In order to avoid this difficulty, the inventors have recognized that it is necessary both to conduct the calculations with the calculated interface and simultaneously to introduce artificial heat sources in order to obtain both the defined interface shape and the correct crystallization rate.

This method is therefore also advantageous because it allows fluctuations in the crystallization rate and in the dopant species around the correct averaged values.

This method can be implemented, for example, with the aid of a modified version of the CGSim software from STR (<https://str-soft.com>).

Four cases have been selected by way of example for the calculations.

The first two cases come from two different processes for crystal diameter 200 mm for arsenic (process A) and red phosphorus (process B). The two further processes are both doped with arsenic and have a crystal diameter of 300 mm, and are referred to hereinafter as process C and process D. The difference between processes C and D
 5 lies in the use of different crystal pulling devices and different pulling speeds, as well as different crystal and crucible rotations.

The inventors have found that the statistically averaged lowest possible resistivities for the processes with 200 mm are 0.9×10^{-3} ohm cm for process A and
 10 1.7×10^{-3} ohm cm for process B. For the processes with 300 mm, these resistivities are 1.75×10^{-3} ohm cm (process C) and 2.1×10^{-3} ohm cm (process D).

All these experimental values are each applicable to a particular position in the crystal, and the calculation cases have been selected in accordance with this one corresponding position.

It should be noted that resistivity values ascertained are average values from many
 15 real experiments and that the results of each experiment are subject to different scatter from process to process and some experiments were unsuccessful, for example because of dislocations.

The specific causal relationship between the occurrence of dislocations and the level of dopant concentrations is unknown to date.

20 Nevertheless, the inventive method gives means of at least avoiding the problem.

The inventors assume that CS could be correlated to these experimental results.

The above-defined parameter CS can be calculated as follows using the Tiller criterion:

$$\frac{CS}{V} = \frac{G_L}{V} - \frac{(1 - k) \cdot C_0 \cdot (-m_l)}{k \cdot D_L}$$

where C_0 - concentration in the melt, k - segregation coefficient, D_L - diffusion coefficient in the melt, V - crystallization rate, G_L - temperature gradient in the melt and m_l - slope of the liquidus line.

5 The parameter G_L can be adopted here, for example, from the corresponding 2D simulations.

According to theory, whenever the condition $CS < 0$ is met, constitutional supercooling would always take place and the correspondingly pulled rod would become unusable.

However, this was found not to be the case. In other words, simple analysis by means of the known Tiller criterion is not possible and hence is unusable.

10 The inventors concluded that further measures are needed.

The inventors recognized that the numerical grid used in all 3D simulations must adequately resolve the concentration interface.

In the simulations, it is preferable that the distance of the closest control volume from the interface of crystal and melt is not more than 0.125 mm.

15 The complete numerical grids in said examples varied from about 3 million control volumes to 3.8 million control volumes.

The result obtained from the 3D simulations is the current distribution of CS values at each position at the interface between crystal and melt. These points are on the crystal rotating above the melt.

20 For the further calculations, CS values that were calculated at points having the same distance from the center of the interface area of the crystal were averaged.

What is thus obtained is a radial distribution of the CS values as a function of time.

In the analysis of the CS values ascertained at different radii, the inventors noticed that the smaller values were apparently more likely to occur in the region of the triple point, and the CS values in the middle of the crystal were relatively unlikely to lie, or lay considerably less often, in the negative region. This would mean that constitutional subcooling supercooling has its starting point at the triple point.

However, experimental findings by Mukaiyama et al. [Y. Mukaiyama, V. Artemyev, K. Sueoka, J. Crystal Growth, 597 (2022) 126844] show by contrast that the consequences of constitutional supercooling are more likely to commence in the center of the crystal.

In spite of this obvious discrepancy, the inventors continued to apply their result and arrived at a method which, with the aid of simulation, predicts possible suitability of a crystal pulling process for a low resistivity.

By this method, it is possible to modify crystal pulling parameters such that crystals having relatively low resistivities can be pulled without loss.

The inventive method of crystal pulling of a monocrystalline crystal from a melt and a dopant by the Czochralski method comprises the following steps:

(a) performing a time-dependent computer simulation of a predefined crystal pulling process with a predefined dopant concentration C in the melt, with the aim of obtaining a temperature gradient $\partial T / \partial n$ and a gradient of the dopant $\partial c / \partial n$ for each time increment t , where the two gradients are ascertained at the interface between crystal and melt in the normal direction of the interface to the melt,

(b) ascertaining a maximum dopant concentration $C_{\max}$ in the melt and

(c) pulling a single crystal with a dopant concentration less than the ascertained maximum dopant concentration $C_{\max}$.

The inventive method additionally includes the calculation of a parameter CS for each time increment t, which is determined by the following formula:

$$CS = \partial T / \partial n - f_{CS} \partial c / \partial n$$

where the parameter f_{CS} is determined by the product of the average concentration of the dopant in the melt, the density of the silicon melt, Avogadro's constant, the molar mass of silicon and the slope of the liquidus line.

Subsequently, an average $\overline{CS}$ over time is formed from the CS values obtained, with a contribution being made only by those CS values that are less than zero. The average over time can be calculated by the formula

$$\overline{CS} = \frac{1}{T_1 - T_0} \int_{T_0}^{T_1} CS(\tau) d\tau, \forall CS(\tau) < 0, \text{ where } T_0 \text{ and } T_1 \text{ constitute the absolute commencement time and end points.}$$

Preference is given to using the average over 30 minutes of physical time or more.

The average $\overline{CS}$ is accordingly a function of the radius and the concentration of the dopant C in the melt. In addition, it is now independent of time.

For the continuation of the method, the average $\overline{CS}$ is selected at one radial position in the crystal. Preference is given here to using the $\overline{CS}$ at the triple point of the crystal, i.e. at the nominal radius of the crystal.

A maximum dopant concentration $C_{\max}$ is ascertained by fitting the dopant concentration C until the magnitude of $\overline{CS}$ = zero, preferably until the magnitude of $\overline{CS} - C_{\text{offset}}$ = zero, where the constant C_{offset} is preferably ascertained experimentally.

The determining of the constant C_{offset}

If the constant C_{offset} is predefined as zero, a lower limit is obtained for the dopant $C_{\max}$, below which it is possible in any case to pull a crystal without yield losses.

In some cases, it may be the case that the lower limit appears too conservative, however, meaning that crystal pulling is possible with a dopant concentration even above this limit.

For such cases, a C_{Offset} is preferably determined with the aid of experimental data as follows.

An empirical limit is ascertained for a crystal pulling process, for example, by pulling one or more crystals, gradually increasing the dopant concentration until the crystal reproducibly has dislocations. This empirical limit ascertained in this way is used to obtain the constant C_{Offset} .

This constant C_{Offset} thus obtained can then be used in order, for example, to compare many different crystal pulling processes and to select that process which has the potential not to generate any dopant-related dislocations. The advantage of this method is that there is no need to conduct any further costly experiments.

More preferably, the constant C_{Offset} is ascertained by testing multiple different processes of a process class, by determining an averaged constant C_{Offset} for each process class in that the individual values are arithmetically averaged.

The inventors have recognized that it can be advisable to define process classes by combining processes having the same process properties to give a process class. These properties are, for example, the nominal diameter of the crystal to be pulled or the use of a magnetic field in crystal pulling. The process class is more preferably defined by processes of the same nominal diameter of the crystals.

Figure 2 shows an example of the sum total of the simulated parameter $\overline{CS}$ and an offset constant C_{Offset} for an example process **A**, shown as a function of resistivity (dashed curve). The limiting resistivity at which the crystal is still just pullable is ascertained by varying the resistivity until the curve of the sum of the simulated parameter $\overline{CS}$ at the triple point of the simulated crystal and the offset constant C_{Offset} becomes zero.

The dark-colored bar drawn in is intended to indicate the resistivity range where there is no prospect of successful crystal pulling.

The dark-colored bar drawn in is intended to show the resistivity range where there is no prospect of successful crystal pulling. There is realistically a small transition region (lightly hatched) in which crystal pulling is possible at high risk, but is inadvisable for economic reasons.

Figure 3 shows the sum of the simulated parameter $\overline{CS}$ at the triple point of the respective crystal and an offset constant C_{Offset} for four example processes (**A** “dashed”, **B** “solid”, **C** “dash-dot”, **D** “dash-dot-dot”), each shown as a function of resistivity.

The respective limiting resistivities at which a crystal is still just pullable have been symbolized by the arrows directed downward on the abscissa axis.

Claims

1. A method of crystal pulling of a monocrystalline crystal from a melt composed of silicon and a dopant according to Czochralski, comprising the following steps in the sequence given:

(a) performing a time-dependent computer simulation of a predefined crystal pulling process with a predefined dopant concentration C in the melt, with the aim of obtaining a temperature gradient $\partial T / \partial n$ and a gradient of the dopant $\partial c / \partial n$ for each time increment t , where the two gradients are ascertained at the interface between crystal and melt in the normal direction of the interface to the melt,

(b) ascertaining a maximum dopant concentration $C_{\max}$ in the melt and

(c) pulling a single crystal with a dopant concentration less than the ascertained maximum dopant concentration $C_{\max}$,

wherein

a parameter CS is calculated for each time increment t , which is determined via the formula $CS = \partial T / \partial n - f_{CS} \partial c / \partial n$,

where the parameter f_{CS} is determined by the product of the average concentration of the dopant C in the melt, the density of the silicon melt, Avogadro's constant, the molar mass of silicon and the slope of the liquidus line,

and then an average $\overline{CS}$ of the values obtained for the parameter CS is formed, where a contribution is made only by those values having a CS value of less than zero,

and a maximum dopant concentration $C_{\max}$ is ascertained by fitting the above-defined dopant concentration C to the magnitude of $\overline{CS} = \text{zero}$.

2. The process as claimed in claim 1, wherein the parameter $\overline{CS}$ is ascertained at the triple point of the crystal.

3. The process as claimed in claim 1 or 2, wherein

a maximum dopant concentration $C_{\max}$ is ascertained by the fitting of the above-defined dopant concentration C until the magnitude of $\overline{CS} - C_{\text{offset}} = \text{zero}$, where C_{offset} is ascertained empirically by pulling one or more crystals, while gradually increasing the dopant concentration until the crystal reproducibly has dislocations.