March 8, 1966 E. SIRTL **3,239,372**

METHOD OF PRODUCING SINGLE CRYSTAL SILICON

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Fig.1

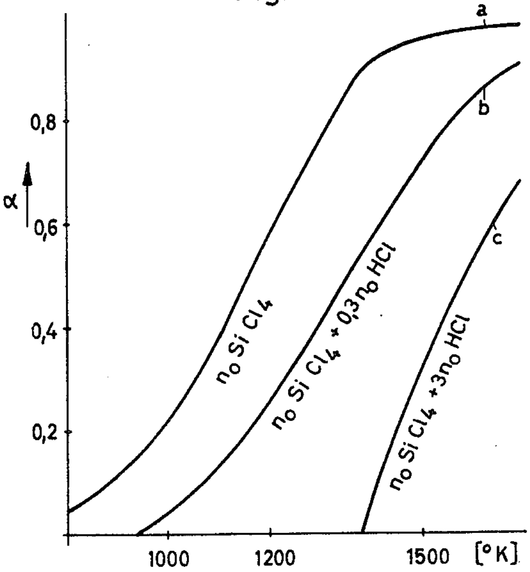

Fig.2

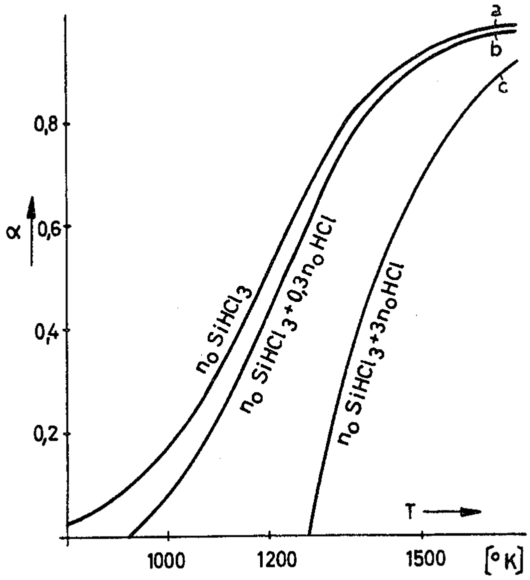

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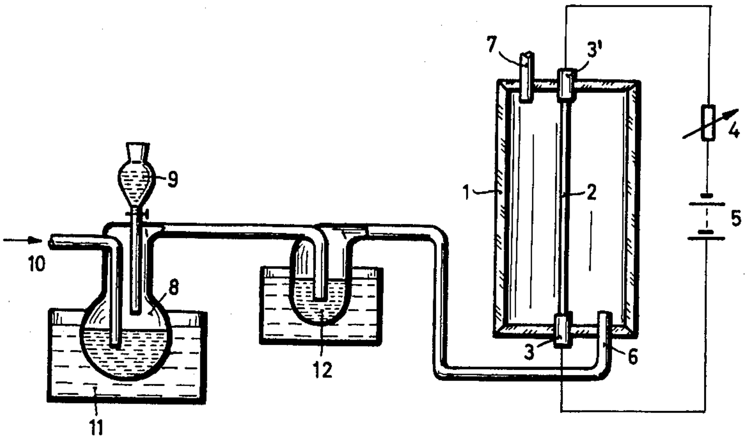
Fig.3



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METHOD OF PRODUCING SINGLE CRYSTAL SILICON

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17 Claims. (Cl. 117—201)

This invention is concerned with a method of producing single crystal silicon and may be considered as a further development on the method disclosed in copending application Serial No. 509,351, filed May 18, 1955, owned by the assignee also named in the present case, and now abandoned.

The prior application describes a method of producing highly pure silicon, utilizing a reaction gas consisting of a purified halogen-containing silicon compound which is preferably intermixed with purified hydrogen, such reaction gas being caused to flow along a carrier body made of hyperpure silicon, which is disposed in a reaction vessel and heated by direct current passage therethrough, thereby causing precipitation upon the carrier body of silicon liberated or separated from the reaction gas by thermal decomposition and crystallization thereon to effect growth of the carrier body. The prior application proposes to use as a carrier a thin elongated silicon rod, especially a silicon wire which is held in the reaction vessel by means of electrodes engaging its ends, and is after preheating thereof caused to glow by the action of electric current conducted thereto over the electrodes. The reaction gas flowing along the hot carrier decomposes due to the heat given off therefrom, liberates or separates silicon which is precipitated upon the carrier and caused to crystallize thereon. The crystal structure of the precipitated silicon is codetermined by the crystal structure of the carrier. Accordingly, there is in principle the possibility of effecting single crystal decomposition by using a monocrystalline carrier.

It has however been found in practice that the single crystal formation is in the prior method quite sensitive to disturbances and that it is without application of auxiliary measures only rarely possible to attain success. It is above all absolutely necessary that the monocrystalline structure of the carrier is upon starting the decomposition process carefully exposed at the decomposition area. This is effected by etching or better, as described in the German application DAS 1,029,941, by subjecting the surface of the single crystal carrier, prior to the decomposition operation, first, to polishing by etching and thereafter highly purifying it by vaporization or steaming in a high vacuum or a suitable protective atmosphere.

It is also recommended to apply the measure described in Patent No. 3,021,198, issued February 13, 1962, likewise owned by the assignee also named in the instant case, and relating to a method and apparatus for producing semiconductor mono crystals, according to which disturbances which could hinder the single crystal growth are in part successfully avoided. The method described in such prior application proposes to heat the surface structure of a monocrystalline carrier body, which had been exposed, for example, by etching, to a temperature lying below the temperature at which is effected the maximum precipitation upon the semiconductor body of the semiconductor substance at the reaction utilized therefor, also, to cause the reaction gas to flow turbulently about the surface of the carrier body and further, to adjust in known manner the decomposition velocity effected at the applied working temperature and reaction, so as to avoid oversaturation of the carrier body with the liberated semiconductor material.

The present invention is concerned with a method of producing single crystal silicon, wherein a flowing reaction gas consisting of a halogen-containing silicon compound, especially halogen silane, preferably intermixed with purified hydrogen, is conducted along an electrically heated single crystal carrier body of pure or doped silicon, which is held in a reaction vessel, to effect precipitation of silicon, separated from the reaction gas respectively by thermal and electrothermal conversion or decomposition, upon the carrier and monocrystalline growth thereof on such carrier.

It is in accordance with the invention proposed to add to the reaction gas at the outset a halogen compound, which is also formed in the reaction gas during the decomposition process, preferably a hydrogen halide, which shifts the reaction equilibrium in favor of the bound silicon, in an amount such that the temperature T_0 of the chemical equilibrium (that is, the temperature at which there is neither silicon separation nor recharging of silicon already present) of the substances which are present in the reaction gas and partake in the separation reaction, lies at the most 200° C. below the applied separation temperature T, and that the silicon separation is completely interrupted below the equilibrium temperature T_0. The equilibrium temperature shall advantageously not lie below 900° C. Accordingly, at areas of the surface of the carrier at which the temperature is below the critical value T_0, there shall not occur a separation but a "dissolution" of the silicon which is present. As will be presently explained more in detail, this offers the possibility of preventing growth at the corresponding areas of the carrier surface.

Irregularities frequently appear, in the absence of particular measures, in the crystal growth in connection with the previously noted separation methods, which result in polycrystalline degeneration of the crystal. It was therefore for a long time practically impossible to produce with such methods silicon monocrystals of relatively large size. It happened, particularly when using $SiHCl_3$ as initial compound, that the surface of the growing crystal showed, corresponding to the prevailing crystal orientation, a wavelike undulating configuration which resulted frequently in a kind of cleavage. Such irregularities must necessarily produce unfavorable effects particularly when it is desired to produce in the growing crystal pn-junctions by coincident separation of doping substances from the gaseous phase. These disturbances in the monocrystalline separation as well as the formation of wartlike protuberances and grooves can be avoided with certainty by sensible application of the method according to the present invention.

The thermal conversion or electrothermal conversion (that is, effected by an electrical gas discharge) of the reaction gas, will as a rule produce, owing to the use, in accordance with the teaching of the invention, of a halogen-containing silicon compound, new halogen-containing compounds which are absent in the initial reaction gas and which upon customary application of a flowing reaction gas generally escape from the reaction vessel with the waste gases. Hydrogen halide substances will primarily appear when using a halogen silane as an initial compound and intermixing therewith a gaseous reduction agent, in practice purified hydrogen, for the purpose of increasing to an economically justifiable amount separation at a temperature lying below the melting point of silicon. The invention proposes, for these reasons, to conduct to the reaction gas primarily a hydrogen compound of the halogen element which is also bound in the silicon compound of the reaction gas that is being used.

Accordingly, upon using chloride silanes, for example, $SiCl_4$, $SiHCl_3$ or SiH_2Cl_2, gaseous hydrogen chloride is preferentially employed as an addition to the reaction gas.

The various objects and features of the invention will now be described with reference to the accompanying drawings, in which

FIGS. 1 and 2 show curves representing amounts of silicon separated from the reaction gas depending upon the surface temperature of the carrier body; and

FIG. 3 shows an example of the apparatus for practicing the invention.

The addition of the substance, for example, HCl, which otherwise forms only in the course of the reaction, produces better equilibrium conditions for the monocrystalline growth of the silicon which is separated from the reaction gas. This can be explained as follows:

It was experimentally established that the separation of silicon from the reaction gas does not normally completely cease even at relatively low carrier temperatures. Upon plotting the amount of silicon separated per unit of time from the reaction gas or the separation velocity α, against the surface temperature of the carrier, there will be obtained curves respectively indicated in FIGS. 1 and 2 at "*a*." The separation curve extends toward the abscissa in a sense asymptotically under a very small angle. However, upon adding HCl, the separation curve will become increasingly steeper in the temperature axis and there will result a well defined intersection point (curves "*b*" and "*c*" in FIGS. 1 and 2) at a temperature T_0.

The reason for this behavior lies probably therein that the reaction equation underlying the separation process extends owing to the presence of the HCl in the reaction gas, below T_0 in opposite sense as in the separation. This means, that silicon is then not separated from the reaction gas, but conversely, silicon that is already present, is dissolved by the reaction gas and thus transferred into the silicon which is present in the reaction gas or as the case may be into other gaseous silicon compounds.

The curves *a*, *b* and *c*, FIG. 1, were obtained with a reaction mixture of 95 mole percent of hydrogen and 5 mole percent of $SiCl_4$ (n_0) (n_0, as used herein, referring to molar concentration employing $SiCl_4$ concentration as the base), which was conducted through the separation apparatus in steady flow. The curve "*b*" was obtained responsive to adding to this reaction mixture 1.5 mole percent HCl ($0.3n_0$), and the curve "*c*" was obtained upon adding thereto 15 mole percent HCl ($3n_0$). The curves *a*, *b* and *c* in FIG. 2 correspond analogously respectively to additions of 5 mole percent and 15 mole percent HCl to a reaction gas flowing through the apparatus in steady flow and consisting of 95 mole percent hydrogen and 0.05 mole percent $SiHCl_3$. All separation curves terminate with growing HCl content increasingly in the temperature axis. Moreover, the temperature T_0 increases with the HCl content of the reaction gas. The curves approach with further increasing temperature respectively saturation and a maximum value.

There is accordingly the possibility, by the HCl addition or variation thereof, to vary the intersection point of the separation curves with the temperature axis, and also to increase at this intersection point the steepness of the tangent with reference to the separation curve. Upon adding to the reaction gas, as contemplated by the invention, hydrogen halide in such an amount that the silicon separation is completely interrupted at a temperature T_0 lying below the temperature of the separation surface of the carrier of at least 900° C., there will be generally obtained a steep separation curve with which a relatively slight temperature increase will effect a considerably greater yield than would be obtained with the same temperature increase in the absence of HCl from the reaction gas and operating in both cases with a temperature which deviates practically only slightly from the temperature at which the separation ceases. On the other hand, if the working point, that is, the operating temperature T is placed into the steep branch of the separation curve, a slight temperature reduction will result in noticeable reduction of the separation which can be carried, contrary to the curve "*a*," to the value 0 and to negative values.

In order to understand the causes for the previously noted disturbances in the crystal growth and therewith the operative effect of the method proposed by the present invention, attention is called to the fact that the carrier is electrically heated. Whether inductive heating is applied or energy is supplied to the ends of the carrier over the electrodes connected therewith, those parts which project from the carrier surface will have the lowest temperature, while recessed areas will be hottest. Accordingly, the protruding parts, for example, wart-like protuberances and the like should responsive to electrical overheating receive less separated material than the recessed parts, for example, grooves or pockets. This is indeed the case, but such compensation is generally insufficient since the protruding parts are preferentially supplied with fresh reaction gas while the recessed parts suffer from a generally considerable unfavorable supply of reaction gas. It follows, therefore, that the quicker growth at parts which protrude or bulge from the carrier surface can be compensated in this manner only incompletely.

It has been observed that the temperature differences between the protruding and the normal carrier surface would amount to over 200° C. In accordance with the invention, care is taken, for this reason, that the separation curve defines a definite intersection point T_0 with the temperature axis. The separation curve is moreover so adjusted that even slight temperature increases above T_0 result in a relatively great yield. Further, the working temperature T of the carrier surface is such that the protruding, that is, the relatively cold parts, receive little separated material until they are evened up and their temperature is approximated to the desired value T. This is assured particularly when the temperature of the relatively cold parts, that is, the protruding parts, is below the temperature T_0, because the separation (precipitation) will not only cease at these parts, but conversely, there will occur a compensation or equalization of these parts and therewith acceleration in the levelling of the carrier surface.

It has been experimentally established that the aim of the invention is fully reached when the temperature T_0 is not below 900° C.–1000° C. and the working temperature not higher than 200° C. above the temperature T_0. It is recommended, for technological reasons having to do with the production, that the monocrystalline rod or wire utilized as a carrier is crystallographically oriented, for example, so that the axis thereof extends in the (1 1 1)-direction.

The working temperatures to be applied in practice as well as the addition of HCl or the like which is to be utilized will aways depend upon the kind of reaction gas that is being used. If the reaction gas is, for example, hydrogen intermixed with $SiHCl_3$ (10 mole percent $SiHCl_3$), it will be advisable to operate with a temperature $T=1110°$ C. to 1200° C., preferably with 1150° C. An addition of 10 mole percent HCl fixes the temperature T_0 at about 950° C.

FIG. 3 shows by way of example an arrangement for carrying out the method according to the invention.

Numeral **1** indicates a quartz vessel in which is disposed a thin rod **2** consisting of hyperpure or doped silicon upon which is to be precipitated respectively hyperpure or doped silicon obtained from a gaseous phase so as to grow thereon in monocrystalline manner. Electrodes **3** and **3'** made of heat resistant material such as graphite, molybdenum and the like, which shall be as pure as possible, serve for holding the rod **2** in place. The rod **2** is held at the separation temperature T, for example, 1150° C., by electric current passing therethrough, which is supplied from a current source **5** over an adjustable stabilizing resistor **4**. The reaction gas enters into the vessel **1** at **6** and the waste gases are discharged at **7**.

A vaporizing vessel **8**, made of quartz, is provided for producing the reaction gas, such vessel containing $SiCl_4$ or $SiHCl_3$ in liquid condition. Into this vaporization vessel extends the extension of a receptacle **9** which contains highly pure distilled water which drops in regulatable manner into the $SiCl_4$ or $SiHCl_3$ contained in the vessel **8**. Some of the silicon halide compound contained in the vaporizaton vessel is thereby hydrolized, thereby producing HCl and silicic acid. Highly purified hydrogen is supplied to the vaporizer **8** at **10** in a regulatable stream and is loaded with the abundantly present vapor of the silicon compound and with the developed HCl, whereupon it is conducted, if desired with further addition of hydrogen, over a cooling trap **12** (for freezing out the water vapors) into the separation vessel **1**. If desired, a further vaporization vessel supplied with $SiCl_4$ or $SiHCl_3$ can be connected serially with or in parallel with the vaporizer **8**, which distinguishes from **8** in that no HCl is developed therein.

The vaporizer or vaporizers are respectively arranged in a temperature bath **11** which is utilized for regulating the rate of vaporization of the silicon compound. The adjustment of the temperature in the vaporizer as well as of the velocity of the hydrogen stream and the amount of distilled water supplied in drops from the receptacle **9**, give the possibility of regulating the composition of the reaction gas in desired and definite manner. The separation curve is by the content of HCl shifted in the described manner so as to fulfill, in cooperation with the surface temperature T of the carrier, the teachings of the invention.

The waste gas discharged from a like or similar separation apparatus for producing silicon crystals respectively from silicon halogen compounds or halogen silanes, can also be utilized as a reaction gas. The reaction gas conducted to the first apparatus, provided that it was in highly pure condition has due to the conversion in the first separation vessel a natural content of the hydrogen halide, so that the waste gas from the first vessel satisfies the requirements posed by the invention with respect to the reaction gas. However, the content of HCl is frequently too slight, making it necessary to add further HCl to the waste gas.

In case other silicon compounds are used, for example, $SiBr_4$ or HBr_3Si, HBr can be substituted for HCl.

Moreover, in the event that more complicated silicon halogen compounds are used, the conversion mechanics of which produces in the separation of pure silicon also other silicon halogen compounds, such secondary silicon compounds can be utilized for improving the monocrystalline growth. However, it will be, generally speaking, possible to obtain the desired object with the corresponding hydrogen halide even in the case of such complicated conditions.

The production of the hydrogen halide content of the initial gas by partial decomposition of a highly pure halogen-containing silicon compound can be effected by hydrolysis or thermal decomposition as well as electrochemically. For example, a fresh mixture of a halogen-containing silicon compound and hydrogen can be partially converted by a stabilized high voltage gas discharge with formation of silicon halides and hydrogen halide, that is, for example, a chloride-containing silicon compound intermixed with hydrogen, and with the formation of silicon subchlorides and HCl. The reaction gas consisting of hydrogen and silicon halide is for this purpose conducted in a steady flow through the gas discharge device and directly therefrom to the separation vessel. The hydrogen halide content of the gas mixture can be adjusted to the desired value by the velocity of the gas stream and the voltage of the gas discharge.

Changes may be made within the scope and spirit of the appended claims which define what is believed to be new and desired to have protected by Letters Patent.

I claim:

1. A method of producing single crystal silicon, consisting of the steps of contacting a carrier body of single crystal silicon with a stream of reaction gas adapted at elevated temperature for the separation of elementary silicon therefrom, heating said carrier body by electric current conducted therethrough to a temperature at which elementary silicon from the reaction gas is precipitated upon the solid surface parts of such carrier body and crystallizing to such surface parts, supplying to said reaction gas as an active ingredient a halogen silane, adding a gaseous hydrogen halide to the reaction gas prior to the contacting thereof with said carrier body, heating the latter during the separation procedure to the separation temperature, adjusting the carrier to a selected temperature at which silicon is separated from the reaction gas with the temperature being such that separation of silicon will be completely interrupted upon dropping of the carrier temperature to at most 200° C. below the selected separation temperature and upon further dropping of the carrier temperatures silicon of the carrier body will be dissolved by the reaction gas.

2. A method according to claim **1**, wherein the reaction gas consists of $SiCl_4$ mixed with hydrogen.

3. A method according to claim **1**, wherein said carrier body is rod shaped, the axis of the carrier having the (1 1 1)-direction.

4. A method according to claim **1**, wherein the temperature below which is effected silicon dissolution from the carrier body instead of silicon separation, amounts to at least 900° C.

5. A method according to claim **1**, wherein the original reaction gas consists of $SiHCl_3$ mixed with hydrogen.

6. A method according to claim **5**, comprising mixing a reaction gas consisting of hydrogen and 10 mole percent $SiHCl_3$ with 10 mole percent HCl, and holding the temperature of the carrier body during the separation process substantially at 1150° C.

7. A method according to claim **1**, wherein the required hydrogen halide content of the reaction gas is produced at least in part by reduction, prior to contact of the reaction gas with the carrier body, of a part of the silicon halogen compound which is present in the highly pure reaction gas with hydrogen.

8. A method according to claim **7**, comprising controlling the reduction of the reduction gas, for the production of the hydrogen halide content, so as to simultaneously produce thereby elementary silicon.

9. A method according to claim **7**, comprising mixing a liquid silicon halogen compound with pure distilled water drop-wise added thereto, so that only part of the liquid halogen compound hydrolizes with water, contacting the resulting mixture with a stream of purified hydrogen gas, the hydrogen being thereby loaded with the vapor consisting of the silicon halogen compound and halogen hydrogen and being together with these vapors conducted into contact with the carrier body.

10. A method according to claim **7**, comprising partially converting a mixture of a silicon halide compound and hydrogen, prior to contact thereof with the carrier body, by applying thereto a layer-stabilized high tension gas discharge with formation of silicon chlorides and hydrogen halide.

11. A method of producing single crystal silicon, wherein a flowing reaction gas which contains a halogenized silane intermixed with purified hydrogen is caused to flow over an electrically heated single crystal carrier body made of pure or doped silicon, which body is disposed in a reaction vessel, the silicon thereby liberated from the reaction gas, respectively by thermal and electro-thermal conversion, being precipitated upon the carrier for single crystalline growth thereon; comprising the following steps, namely, admixing with a reaction gas, prior to conducting it into the reaction vessel which contains the heated carrier body, a gaseous hydrogen halide in such amount that silicon separation is obtained at the carrier surface at an adjusted predetermined carrier temperature which is maintained during the separation process, while the silicon separation is completely stopped upon decrease of the carrier temperature to a point lying at the most 200° C. below the adjusted temperature value and, upon further decrease of the carrier temperature, dissolving, by the reaction gas, of precipitated silicon will take place.

12. A method according to claim **11**, wherein the hydrogen halide content of the reaction gas is produced by corresponding partial conversion of a highly pure hydrogen silane.

13. A method according to claim **11**, wherein the temperature, at which the silicon separation is completely stopped and below which silicon already present would be dissolved, amounts, due to appropriate composition of the reaction gas to be conducted into the separation vessel, to at least 900° C., and wherein the temperature at the surface of the carrier is adjusted to a value which is higher by at the most 200° C.

14. A method according to claim **12**, wherein the waste gases, containing hydrogen halide, from an arrangement for producing highly pure silicon from a halogen silane, are utilized as a basis for the reaction gas.

15. A method according to claim **12**, comprising conducting purified hydrogen to a vaporization vessel filled with liquid halogen silane, producing in said vessel a hydrogen halide by feeding purified water thereinto in the form of drops, and thereupon conducting into the reaction vessel the hydrogen loaded with the hydrogen halide and vaporized residual halogen silane which has not been decomposed.

16. A method according to claim **12**, comprising conducting, prior to the silicon separation, a fresh mixture of halogen silane and hydrogen through a layer stabilized high tension gas discharge, whereby the fresh mixture is partially converted with formation of silicon subchlorides and HCl.

17. In the method of producing hyperpure semiconductor material, selected from the group consisting of silicon and germanium, for electronic purposes by pyrolytically precipitating said material, from a gaseous reaction mixture of a compound thereof mixed with a reducing gas, onto a monocrystalline carrier body of the same material within a closed reaction vessel, the improvement which comprises adding the hydrogen chloride contained in the waste gas of the same process to the reaction mixture supplied to the reaction vessel to thereby promote monocrystalline growth on the monocrystalline carrier body.

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