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(71) Applicant (for all designated States except US): **GIRA-SOLAR B.V.** [NL/NL]; Leeuwenbrug 119A, NL-7411 TH Deventer (NL).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **DOBBERSTEIN, Uwe, Hermann** [DE/NL]; Putmanstraat 42, NL-7415 TP Deventer (NL).

(74) Agents: **DOHMEN, Johannes, Maria, Gerardus et al.**; Algemeen Octrooi-en Merkenbureau, P.O. Box 645, NL 5600 AP Eindhoven (NL).

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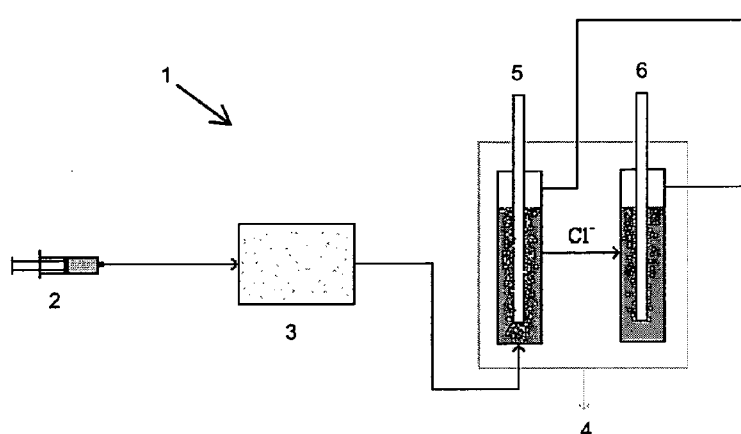
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(54) Title: METHOD FOR THE PURIFICATION OF A SEMICONDUCTOR MATERIAL BY APPLICATION OF AN OXIDATION-REDUCTION REACTION



(57) Abstract: A method for the purification of a semiconductor material, the method comprising the steps of: a) the oxidation at an anode, which is placed in an anodic electrolyte, of a solid semiconductor material to be purified by application of one or more ionic compounds; b) the reduction at a cathode, which is placed in a cathodic electrolyte, of one or more compounds obtained in step a), to a purified, solid semiconductor material where one or more ionic compounds are also formed; where the one or more ionic compounds that are formed in step b) are applied in step a) and the anode and cathode are mutually connected for electron transfer. The formed ionic compounds are purified externally. The present method can for example be applied for the purification of silicon.

Method for the purification of a semiconductor material by application of an oxidation-reduction reaction

DESCRIPTION

The present invention relates to a method for the purification of a semiconductor material by application of an oxidation-reduction reaction.

Silicon is one of the best known and most applied semiconductor materials and is often applied in the industry, such as for example in solar cells, diodes, transistors, integrated circuits (chips) and other areas of electronics. For such applications, a high purity or silicon is required, such as for example so-called SoG silicon (Solar Grade, purity of > 99.9999% (> 6N)) or EG silicon (Electronic Grade, purity of > 99.9999999% (> 9N)). So-called MG silicon (Metallurgic Grade, purity of 98 - 99%) is often applied to obtain such pure silicon. Such silicon materials are generally obtained from SiO_2 (for example, sand) by reduction with carbon (C) under formation of carbon mono oxide (carbothermal reduction).

Examples of impurities that may be present in MG silicon are carbon, boron or phosphorus compounds and metallic elements, such as for example iron, aluminium, titanium and vanadium. Among other things, such impurities cause a deterioration of the semiconductor properties of the material, which for example may lead to a reduced yield for solar cells. Furthermore, such deteriorated semiconductor properties are also undesirable for other electronics applications.

Certain impurities, such as for example iron, aluminium, boron, phosphorus, titanium and vanadium are more deleterious than others and in addition, certain impurities are more difficult to remove from silicon than others. The simplicity of removal is related to, among other things, the separation coefficient or the difference in solubility of a certain element in fluid and solid silicon.

The standard process for the purification of silicon that is currently applied consists of a number of steps, namely a first step in which MG Si is chlorinated with HCl gas to 90% SiHCl_3 (trichloro silane) and 10% SiCl_4 (silicon tetrachloride) during which process hydrogen gas is formed.

Subsequently, the newly formed silicon compounds in the gas phase are purified by means of fractional distillation until the quantity of impurities reaches the ppb (parts per billion) and ppm (parts per million) level.

In a next step, the so-called 'Siemens process', deposition of purified silicon takes place by application of the purified gaseous silicon compounds and hydrogen. This reaction is carried out at a temperature of for example 900-1100 °C on an electrically heated graphite electrode to form polycrystalline silicon of a purity of 99.99999% (7N) and HCl. A similar method for the purification of silicon is disclosed in US patent 4,213,937.

The disadvantage of such a method is firstly, that a corrosive gas such as HCl and an explosive gas such as hydrogen are required for the reaction, which puts high demands on the applied equipment and safety requirements. Secondly, the process is highly energy-consuming because of the thermal processes that take place in the conversion of silicon compounds to crystalline silicon.

The electrochemical deposition of silicon on a silicon cathode by application of silicon tetrachloride (SiCl_4) as starting material is known from T. Matsuda et al., Chemistry Letters, 1996, page 569-570.

The electrochemical synthesis of silane (SiH_4) from MG silicon by application of hydrogen gas is known from T. Nohira et al., Electrochemistry, 2005, 73(8), page 692-699.

JP 06/173064 discloses a method for the electrolytic purification of titanium by means of electrolysis in molten salts.

WO 02/099166 discloses a method for making silicon by dissolution of SiO_2 in an electrolyte consisting of CaCl_2 and CaO .

It is an objective of the present invention to provide a method for the purification of semiconductor materials that is energy-efficient.

It is also an objective of the present invention to provide such a method in which no corrosive or explosive gases are required.

In addition, it is an objective of the present invention to provide such a method that can be carried out with simple equipment without stringent safety regulations.

One or more of the above objectives are attained by the method according to the preamble, characterised in that the method comprises the steps of:

a) the oxidation of an anode placed in an electrolyte and made of a semiconductor material containing one or more impurities, one or more ionic compounds being present in the electrolyte, and the ionic compounds reacting with

the semiconductor material and the one or more impurities, to form one or more compounds according to formula I:



where A = ion of semiconductor

X = halogen ion

H = hydrogen

y = valence of A

z = integer greater than or equal to 1

and one or more associated reaction products.

b) the addition of one or more compounds of formula I, obtained in step a), at a cathode placed in an electrolyte and the carrying out of the reduction there to form purified semiconductor material on the cathode, one or more ionic compounds also being formed in this reduction;

where the one or more ionic compounds formed in step b) are returned to step a) and the anode and cathode are mutually connected for electron transfer.

The present invention will be further explained on the basis of silicon as example of a semiconductor material; however, the present invention is also applicable to other semiconductor materials such as for example germanium.

The present invention will also be explained on the basis of the drawings:

Figure 1 is a schematic representation of a configuration that has been applied to carry out the method according to the present invention;

Figure 2 is a schematic representation of an electrolytic cell that can be applied for carrying out methods according to the present invention;

Figure 3 is representation of a cyclic voltammogram;

Figure 4 is a SEM-EDX graph; and

Figure 5 is a SEM-EDX graph.

In the present method, two half-reactions are coupled, namely an anodic reaction in which impure silicon is converted into halogenated silicon compounds and a cathodic reaction in which purified halogenated silicon compounds are converted into purified silicon.

The present invention provides an energy-efficient method by carrying out a first reaction (step a according to the present method) at an anode and the second reaction (step b according to the present invention) at a cathode. The electrons that are formed at the anode are used at the cathode as a result of which, in principle, no additional energy is required, as a reversible (equilibrium) reaction is used. The supply of additional energy by increasing the electrical difference of potential can accelerate the reaction significantly.

A further advantage of the present invention is that HCl gas and hydrogen gas are no longer required, as ionic compounds, such as for example chlorine ions or other ions, can be applied instead of gaseous compounds. These ionic compounds will react with the semiconductor material of the anode to form the compounds according to formula I, such as for example halogenated silicon compounds if a silicon anode is applied. Thus, one or more of the above objectives are attained.

In addition, the one or more impurities present in the semiconductor material to be purified react in one or more reactions with the one or more ionic compounds to form the associated reaction products. Such associated reaction products, if MG-Si is applied as anode, are for example FeCl_3 , PCl_3 , BCl_3 , TiCl_4 , AlCl_3 and VCl_4 .

The electrolyte serves as transport medium for the ionic reaction products from the cathode to the anode. Returning these ionic reaction products therefore preferably takes place through the electrolyte.

The addition to the cathode of the one or more compounds according to formula I can for example take place by bubbling such compounds as a gas at the cathode. However, other methods can also be applied.

Figure 1 shows an example of a configuration 1 which was used by the present inventors for carrying out the method according to the present invention. Figure 1 displays a syringe pump 2, connected to an evaporation device 3, this evaporation device 3 being connected to an electrolytic cell 4.

A cathode 5 and an anode 6 are present in the electrolytic cell 4, displayed in Figure 1. Ion exchange takes place between the cathode 5 and the anode 6, displayed in Figure 1 by an arrow next to which Cl^- is written.

According to step a) of the present method, one or more ionic compounds are formed at the anode 6 and are collected (see arrow at anode 6).

These compounds are subsequently purified externally. The purified desired silicon compounds are subsequently supplied to the cathode for carrying out step b) of the present method, by application of the syringe pump 2. Any unreacted silicon compounds are drained off in the form of gas at the top of cathode 5 (see arrow at cathode 5).

Figure 2 is an embodiment of an electrolytic cell applicable in the present invention. This preferred embodiment of the electrolytic cell 4 consists of a quartz tube 7 which is closed on one end and which is partly filled with electrolyte 8. Two quartz tubes 9 having open lower ends are placed in this electrolyte 8. The anode 6 and the cathode 5, respectively, have been placed in these quartz tubes. In this way of addition of the anode and cathode to the quartz tubes 9, it is possible to separate the anode 6 and cathode 5 from one another as a result of which vapour released at the cathode 5 and anode 6 can be separated individually. Also displayed is a quartz tube with a reference electrode 10 as well as a quartz tube with a thermo couple 11 to measure the temperature as well as a supply pipe for compounds in the form of gas.

It is preferred that the formed compounds according to formula I are purified according to the present invention. This can take place by a preferable embodiment of the present method, comprising an additional step c) that is carried out after step a) and before step b) where step c) comprises two sub steps, c1) and c2), namely

c1) the extraction of the one or more compounds according to formula I and the one or more associated reaction products from the electrolyte;

c2) the separation of the one or more compounds according to formula I from the one or more associated products.

Thus, in the case of MG-Si as anode in this embodiment, both the formed halogenated silicon compounds and the associated reaction products are extracted, preferably as gas, from the electrolyte in which the anode has been placed and are, after purification thereof, added to the cathode where reduction can take place to form silicon and ions (for example chlorine ions). The ions preferably move, through the electrolyte, to the anode where they react with MG Si to form additional halogenated silicon compounds.

Such an embodiment of the present invention ensures excellent purification and prevents contamination of the electrolyte. Impurities possibly

present in the starting material, such as for example boron and phosphorus, are removed before the purified halogenated silicon compounds result in pure silicon by deposition on the cathode. Specifically the removal of boron and phosphorus is of great importance as these elements are applied as dopants in the further processing of pure silicon. The quantity of such dopants should be determined very accurately to obtain the desired properties and therefore, it is of great importance that these elements are present in the purified silicon as little as possible.

Step c1) may for example be carried out by means of phase separation. Halogenated silicon compounds are volatile at the applied temperatures and may therefore be collected as gases from the fluid electrolyte. Other extraction methods, however, may also be applied.

Step c2) may for example be carried out by means of fractional distillation. The halogenated silicon compounds and the halogenated impurities possess different boiling points and may therefore be separated by means of distillation. Other separation methods, however, may also be applied.

It is preferred that the compounds according to formula 1 are separated in step c2) until they possess a purity of greater than or equal to 99.99% (4N), preferably 99.999% (5N), in particular 99.9999% (6N) and more specifically 99.99999% (7N). The desired purity will depend on the desired application, such as already explained previously.

In particular, silicon is applied as the semiconductor material in step a), and more specifically MG silicon, because of the good availability of the latter.

The material of the cathode is preferably selected from the group consisting of silicon, carbon, silver, molybdenum, platinum and tungsten and one or more combinations thereof. However, other conducting materials are also applicable. In particular, silicon and more specifically silicon of at least the desired purity, that is, a purity of greater than or equal to 99.99% (4N) and preferably 99.9999% (6N), are preferred as cathode material.

Such materials give sufficiently good properties regarding electron conductance and are inert. These materials have a low resistance to electron conduction at the operating temperature, give minimum contamination of the silicon to be purified, minimum contamination of the electrolyte and contain surface sites with low activation energies for the simple crystallisation of silicon.

The advantage of the application of silicon as cathode material and

more specifically of silicon of at least the desired purity is that it is simpler to remove the formed silicon from the cathode, for example by scraping it off, without formation of any impurities in the formed silicon because of also scraping off cathode material.

The anode material preferably consists of semiconductor material to be purified, where it is possible that the semiconductor material to be purified forms the entire anode, that is, that the anodes for example consist of a wire, rod or chunks of MG silicon. It is also possible that the anode consists of a core of an inert material, which serves as carrier, the inert material preferably not being a conductor for electrons, and the inert material being enclosed in a mantle of the semiconductor material. Such a mantle may for example be applied to the core by means of deposition, sputtering or coating.

Specifically preferred is that the semiconductor material to be purified is porous or pulverulent. As a result, the material to be purified possesses a large surface area, which increases the reaction rate.

In the method according to the present invention, two electrolytes are applied, more specifically an electrolyte in which the anode has been placed and an electrolyte in which the cathode has been placed. It is preferred that these electrolytes are identical. This makes the reactor design simpler as the anode and the cathode can be present in a single vessel. This also simplifies returning the ionic compounds from the cathode to the anode.

The electrolyte in which the cathode has been placed preferably meets the following requirements:

- high ion conductance (low resistance) to minimize energy loss caused by resistance and to realize mass transfer of the formed ionic compounds;

- higher standard reduction potential (E_0) than the compounds according to formula I to prevent electrolysis of the electrolyte; a high standard reduction potential is preferred as this allows the application of greater differences of potential across the electrodes (see also hereafter) as a result of which the reaction rate increases;

- low solubility of the semiconductor material formed on the cathode to prevent its loss in the electrolyte;

- low solubility and diffusion rate in the semiconductor material formed on the cathode to prevent its contamination;

- high solubility in water to enable simple removal of the electrolyte

during rinsing of the semiconductor material formed on the cathode.

The electrolyte in which the anode has been placed preferably meets the following requirements:

- high ion conductance (low resistance) to minimise energy losses caused by resistance and to realize mass transfer of the formed ionic compounds;

- high standard reduction potential (E_0) to prevent electrolysis of the electrolyte;

- low solubility for the anode material to prevent contamination of the electrolyte, as such contamination of the electrolyte may lead to contamination of the semiconductor material formed on the cathode;

- low solubility of compounds according to formula I and associated reaction products to simplify extraction thereof;

- low solubility of associated reaction products to prevent contamination of the electrolyte.

As electrolyte, for example molten salts can be mentioned. It is preferred that the electrolyte is a salt of one or more halogens and one or more alkali (earth) metals or one or more combinations thereof, such as NaCl, KCl, LiCl_2 and BaCl_2 but also nitrates, carbonates and sulphates and combinations thereof or ionic fluids at room temperature can be mentioned as electrolyte. Such electrolytes can be applied both as electrolyte in which the anode has been placed and as electrolyte in which the cathode has been placed.

In one embodiment of the present invention, a membrane is applied that is permeable to the one or more ionic compounds that are formed in step b). The membrane is present between the electrolyte in which the anode has been placed and the electrolyte in which the cathode has been placed.

Such a membrane should be selectively permeable for the passage of ionic reduction compounds from cathode to anode and not to oxidation products from anode to cathode. A membrane may prevent contamination of the electrolyte in which the cathode has been placed, such contamination possibly consisting of positively charged ions (metal and other) that may be deposited on the cathode and therefore contaminate the purified semiconductor material.

The membrane is preferably made of a ceramic material, such as for example La-M-O-Cl (M is alkali earth metal, such as for example Ca/Sr). Such a ceramic material is an example of a so-called 'Solid Electrolyte' which is applied in

fuel cells.

It is also possible that a capture electrode is applied which is connected to an external voltage source, the capture electrode having an equal or somewhat higher potential relative to the cathode, and the capture electrode having been placed in the electrolyte between the anode and the cathode.

The capture electrode is not exposed to the compounds according to formula I that are added to the cathode and the sole purpose of this capture electrode is to provide a site for precipitation and adherence of impurities (oxidation products) that are released at the anode.

In one embodiment of the present invention, additionally one or more compounds according to formula I are added in step b) to compensate for any possibly observed losses during the purification according to step c2). Such compounds should be of the desired purity, that is, a purity of at least 99.99% (4N) and more specifically at least 99.9999% (6N).

The conditions for carrying out the present reaction, such as pressure, temperature and reduction potentials, are determined by the reaction rate of the anodic and cathodic reactions.

Hereafter, the reaction conditions are written for when silicon is applied.

Cathodic reaction conditions

It is preferred to obtain crystalline, purified silicon. The minimum temperature for the precipitation of silicon around the electrode is circa 400 °C caused by the conductive behaviour of silicon which increases with increasing temperature, as is usual in semiconductors. The transition from amorphous to crystalline silicon occurs at a temperature of 470 °C and therefore, the temperature at the cathode is preferably at least 400 °C, more specifically at least 470 °C. In principle, it is also possible that amorphous silicon is formed at the cathode which for a certain temperature of the cathode, for example a temperature above 470 °C, is subsequently converted to crystalline silicon. For certain applications, amorphous silicon as such can also be applied.

Crystalline silicon can also be formed at a lower temperature (< 400 °C) by using the high resistance of silicon at low temperature, which leads to local heating of the cathode which leads to formation of crystalline silicon. If the resistance rises, the temperature will also rise and this will lead to an improved

crystalline form of for example silicon. A higher resistance will, however, also lead to an increased energy usage which is disadvantageous. It is therefore of importance to find a good compromise.

To obtain a high deposition rate of silicon and therefore a high reaction rate, the concentration of the compounds of formula I at the cathode should be as high as possible. In the case that halogenated silicon compounds are applied, these are gaseous at the application temperature of at least 400 °C because of their boiling points and therefore, the reaction will be carried out in three phases, namely solid (cathode), fluid (electrolyte) and gaseous (halogenated silicon compound).

The pressure should preferably be high to enable a high concentration of the compounds according to formula I. If the halogenated silicon compounds are added to the cathode as gas (bubbling), the electrolyte should possess a surface tension as high as possible and the bubbles should be as small as possible to obtain an internal pressure as high as possible. This is because the internal pressure in a gas bubble is determined by the external pressure of the fluid and the surface tension divided by the radius of the bubble.

If a membrane and/or capture electrode is applied, the conditions such as temperature and pressure should be adjusted accordingly.

Anodic reaction conditions

It is desirable that all products that are formed at the anode are gaseous to limit contamination of the electrolyte to a minimum. Whether the products that are formed at the anode are gaseous depends on the temperature and pressure that are applied, in combination with the boiling points of such formed compounds.

To obtain gaseous products, the boiling point of the formed compound should be lower than the temperature at which the reaction is carried out. For example, the boiling point is 57.6 °C for the desired SiCl_4 which will be gaseous at the reaction temperature. Examples of contaminants often present in MG Si that are gaseous at a reaction temperature of 400 °C are the following: BCl_3 (12.5 °C), PCl_3 (75.95 °C), TiCl_4 (136.4 °C), PCl_5 (160 °C), AlCl_3 (182.7 °C) and FeCl_3 (315 °C). At a reaction temperature of 400 °C, such by-products will be released as a gas and these by-products will therefore not lead to problems during the purification. However, FeCl_2 which also often occurs in the reaction has a boiling point of 1026 °C and thus will not be collectible as a gas at a temperature of 400 °C and should

therefore be removed by some other way. To this end, for example a membrane or capture electrode is required.

It is preferred that an external voltage source, which is not limited to a certain type, is applied to apply a difference of potential across the anode and the cathode, the difference of potential being selected between 0.01 V and the standard reduction potential of the electrolyte.

Only very little energy is required for the actual carrying out of the present reaction because a reversible reaction is applied between the semiconductor and the compounds according to formula I. In theory, this would correspond to a difference of potential of 0 V. However, in practice, this would last indefinitely as there is no driving force for the reaction. To be sure that the reaction rate is sufficiently high to be practically applicable, a difference of potential of more than 0 V should be applied, such as for example more than 0.01 V. The difference of potential should not exceed the standard reduction potential of the applied electrolytes to prevent their electrolysis. It is preferred that the difference of potential is as high as possible as is allowed with the applied electrolyte. Therefore, it is preferred to apply an electrolyte with a high standard reduction potential to enable a high reaction rate.

The reduction potential (E_0) of SiCl_4 is -1.451 V at 25 °C and is -1.389 V at 850 °C. The reduction potential of a number of the previously mentioned electrolytes is as follows: MgCl_2 (-3.066 V at 25 °C and -2.42 V at 850 °C), CaCl_2 (-3.887 V at 25 °C and -3.296 V at 850 °C), NaCl (-3.982 V at 25 °C) and KCl (-4.235 V at 25 °C). The applicability of electrolytes depends on the mobility of the ionic compounds in the electrolyte.

In one embodiment according to the present invention, the electrolyte is forced to flow from the cathode to the anode and vice versa. In such an embodiment, the electrolyte is led, at a particular rate, in a flow from the cathode and the anode, and in particular, the flow of the electrolyte from the anode to the cathode is physically separated from the flow of the electrolyte from the cathode to the anode. This is, for example, possible by a closed loop whereby the electrolyte is forced to flow and where the anode and cathode have been placed in the closed loop at individual sites. More specifically, it is advantageous when a membrane or in particular a capture electrode has been placed between the anode and the cathode.

The advantage of such a construction is that when the flow rate is

sufficient, the purification of the electrolyte will be simplified. Cations present in the electrolyte want to go to the cathode and are created at the anode. Because of the flow, they can only go by the route in which the membrane/ capture electrode is present. The cations can, at a particular flow rate, not go against the flow and will therefore always be forced to go past the membrane or the capture electrode. A capture electrode is preferred over a membrane because a capture electrode neutralizes cations and a membrane only captures cations.

Such a circulation of the electrolyte may for example be realised by application of a pump or by application of a density difference. A density difference may for example be realized by a temperature difference but also by the presence of gas bubbles (bubbling) at an electrode, such as the cathode. However, other methods for the realization of a circulation flow may also be applied.

An additional example of the application of circulation is that in the case that chlorine ions are present, they will not be only transported to the anode by diffusion and that better matter transfer will take place at the electrode by the flow, as a result of which higher conversion rates are obtained.

The present method may be carried out by application of any suitable equipment or combinations thereof, such as for example a device for processing of MG silicon (crushing, leaching), an electrolytic cell (anode and cathode and electrolytes), a separation device for purification of halogenated silicon compounds (distillation, absorption, absorption, membrane separation) and a device for processing pure silicon (washing, crushing).

The present invention will now be further explained on the basis of the following, non-limiting example.

Example

A configuration was applied such as displayed in Figure 1. A syringe pump from KD Scientific, model KDS200 with a polypropylene syringe of 30 ml was applied as syringe pump. This syringe pump was filled with purified SiCl_4 in the fluid phase and set to a syringe rate of 0.5 ml/minute. For testing purposes, SiCl_4 was used which was obtained from VWR, The Netherlands of a purity of > 99%. However, when carrying out the entire method, the SiCl_4 will be formed at the anode and will be returned to the cathode after possible extraction and purification.

The SiCl_4 is transferred, by the syringe pump and Teflon tubes, to the inlet of an evaporation device, consisting of a container with a volume of 3 litres,

made of boron silicate and provided with a cover with inlet and outlet. The cover is closed airtight by means of an O-ring and is subsequently, with the exception of the bottom, fully insulated with glass fibre mats. The container's bottom is placed on a hot plate with a constant temperature of 200 °C.

5 A valve has been placed between the syringe pump and the evaporation device so that, if necessary, the syringe can be replaced without this affecting the pressure in the evaporation device. The outlet of the evaporation device is connected to the electrolytic cell by an insulated tube of boron silicate. The purpose of the evaporation device is to evaporate the SiCl_4 for introduction into the reactor to prevent flash evaporation in the reactor.

10 The electrolytic cell according to the present example is as displayed in Figure 2. The diameter of the external quartz tube is 60 mm and this external quartz tube has a total length of 400 mm. The electrolyte is added in such a way that it fills one third part of the reactor.

15 The electrolytic cell was placed vertically in an electrical oven, which can be heated to 1200 °C, where the top of the electrolytic cell has been placed outside the oven. The oven is an electrical oven obtained from Westeneng Ovenbouw, The Netherlands and had a simple control unit which makes it possible to set the temperature prior to the reaction.

20 In this example, the anode has been made of two strips of n-type silicon of electronic purity, doped with phosphorus, with a resistivity between 1 and 30 ohm.cm. The purity of this material was greater than 99.9999%. The strips are approximately 1 cm wide, 15 cm long and 1 mm thick. In each strip, there is a recess on one end which was applied for attaching the strips to the end of a tungsten rod (2 mm diameter) by application of platinum wire. The other end of the tungsten rod was connected to the potentiostat as counter electrode. Before the anode was allowed to sink into the electrolyte, the silicon part of the anode was immersed in a 10% HF solution to remove any oxides from its surface. It will be clear that only the silicon part of the anode is in contact with the electrolyte. The total anode area that was exposed to the electrolyte was at least 42 cm².

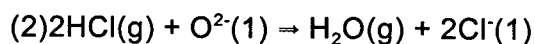
25 The cathode has been made of tungsten (length 400 m, diameter 2 mm), immersed in the electrolyte. SiCl_4 , which serves as starting material, was supplied as a gas along the surface of this cathode. The tungsten electrode had a total reaction area of approximately 11 cm². The other end of the rod was connected

to the potentiostat as a working electrode. The pseudo reference electrode was a platinum wire with a diameter of 0.5 mm with an active reaction area of approximately 0.75 cm².

The electrolyte was a eutectic mixture of 50 mole percent KCl (99.5% purity) and 50 mole percent NaCl (99.5% purity) with a melting point of 650 °C. The total salt mass that was applied in the electrolyte was 880 g. The salt mixture was placed in a quartz reactor tube and heated to a temperature of 810 °C to melt. After melting, the oven temperature was set to a temperature of 710 °C and the electrolyte was kept at this temperature for the entire duration of the experiment. Before the electrodes were allowed to sink into the electrolyte, any dissolved oxides in the melt were removed by the addition of a small quantity of NH₄Cl (99% purity). The KCl, NaCl and NH₄Cl were all obtained from VWR, The Netherlands.

The potentiostat with 3 electrodes was of the type PAR-273-A, manufactured by EG&G Princeton Applied Research, and was computer-controlled with the LabVIEW programme. This was applied to carry out cyclic voltammetric tests on the electrolytic cell. All experiments were carried out in an atmosphere of argon gas and any vapours that are released at the electrodes are condensed. Any not condensed gas was led through water to neutralize any SiCl₄ still present in it.

The present inventors found that more specifically the application of NaCl and KCl as a eutectic mixture gives excellent results. The same above experiment was also carried out by application of CaCl₂; however, it was found that this leads to erosion and corrosion of the quartz reactor because of the strong solubility of O²⁻ ions. Therefore, the mixture of NaCl/KCl was selected as this has only limited solubility for O²⁻ ions. To remove any O²⁻ ions that are present in the melt, NH₄Cl salt was added. NH₄Cl salt decomposes at high temperature according to equation 1 which is displayed hereafter. The HCl that is formed may react with any O²⁻ ions according to reaction 2, where the O²⁻ ions are removed from the melt.



A cyclic voltammetric experiment was carried out, firstly without SiCl₄ present to determine the background of the experiment. Measurements were subsequently carried out with a SiCl₄ gas flow that was supplied by means of the

syringe pump and the evaporation device. The results of these measurements are displayed in Figure 3.

In all cases, the voltage was changed between 0 and -3V with regard to the platinum pseudo reference electrode. A scan rate of 5 mV/s was applied in both cases.

In the case that no SiCl_4 was present (black curves), the current increased very strongly when the difference of potential became more than -2.2V with regard to the Pt electrode. It is assumed that this peak corresponds to electrolysis of the electrolyte with formation of Cl_2 (or SiCl_4 on the anode) and precipitation of K and Na on the cathode. Sodium will be deposited first as this has a lower reduction potential than potassium. The scan was repeated four times with similar results for each scan.

Subsequently, SiCl_4 gas was supplied to the system and current peaks were observed in the area between -1.2 and -1.7V (grey curves). It is assumed that these peaks correspond to the reduction of SiCl_4 to Si on the cathode, which is the desired reaction. To be certain that sufficient silicon will be deposited to obtain sufficient sample for analysis, repeated scans were carried out by changing the potential between -1.2V and -1.7V while SiCl_4 is added to the reactor. This was carried out for 1.5 hours before the entire system was switched off, the electrodes were removed and the electrolyte was allowed to cool and solidify.

A thin layer of material was observed on the tungsten electrode, while also observed was that the silicon anode contained a number of pits. A part of the unreacted SiCl_4 that is released at the cathode was condensed. Only a small quantity of condensation was observed from the anode but not sufficient to have a sample of it examined. Also observed was that a black deposit is formed on the electrolyte that precipitates on the bottom of the quartz tube. Moreover, pieces of the tungsten electrodes as well as pieces of the electrolyte containing black deposit were analysed by TNO (Dutch organisation for applied natural sciences research) by application of SEM-EDX. The EDX analysis of the tungsten cathode is displayed in Figure 4. It is observed that the electrode contains high levels of both tungsten, which is to be expected according to the present method, and silicon, which is deposited on the electrode. Furthermore, small quantities of impurities are present. From this analysis, it can be determined that a silicon layer is indeed deposited on the tungsten cathode.

The electrolyte parts with black deposit were dissolved in water and washed to obtain a black powder which was analysed. The EDX analysis of the black powder is displayed in Figure 5. The analysis shows that the powder is largely pure silicon with very small quantities of sodium from the electrolyte. It is possible that this sodium was deposited during the electrolysis of the electrolyte to determine the background. It was assumed that the silicon powder had a porous structure with a particle diameter of approximately 50 μm .

By the above experiment, it can be shown that by application of the present method, it is possible to deposit a significant quantity of silicon on the cathode and as a porous powder by the electro reduction of SiCl_4 gas on a cathode placed in a molten electrolyte of a chloride salt. It was also observed that the silicon anode corroded during the experiment to provide a condensable vapour of silicon chloride.



CLAIMS

1. A method for the purification of a semiconductor material by application of an oxidation-reduction reaction, characterized in that the method comprises the steps of:

a) the oxidation of an anode placed in an electrolyte, which anode is and of a semiconductor material containing one or more contaminations, the electrolyte having one or more ionic compounds present, and the ionic compounds reacting with the semiconductor material and the one or more impurities to form one or more compounds according to formula I:



where A = ion of semiconductor

X = halogen ion

H = hydrogen

y = valence of A

z = integer greater than or equal to 1

and one or more associated reaction products,

b) the addition of the one or more compounds of formula 1, obtained in step a), to a cathode placed in an electrolyte and carrying out the reduction there to form purified semiconductor material on the cathode, the reduction also leading to formation of one or more ionic compounds;

where the one or more ionic compounds formed in step b) are returned to step a) and where the anode and cathode are mutually connected for electron transfer.

2. A method according to claim 1, where the method comprises an additional step c) which is carried out after step a) and before step b) where step c) comprises two sub steps, c1) and c2) namely

c1) the extraction of the one or more compounds according to formula I and the one or more associated reaction products from the electrolyte;

c2) the separation of the one or more compounds according to formula I from the one or more associated products.

3. A method according to claim 2, where in step c2) the one or more compounds according to formula I are separated to a purity of greater than or equal to 99.99% (4N), preferably 99.9999% (6N).

4. A method according to any one or more of the preceding claims, where silicon is applied as the semiconductor material in step a).

5. A method according to claim 4, where MG silicon (metallurgical purity) is applied as the semiconductor material in step a).

6. A method according to any one or more of the preceding claims, where the material of the cathode is selected from the group consisting of silicon, carbon, silver, molybdenum, platinum, tungsten and one or more combinations thereof.

7. A method according to claim 6, where silicon of a purity of greater than or equal to 99.99% (4N), preferably 99.9999% (6N) is applied as the cathode.

8. A method according to any one or more of the preceding claims, where a core of an inert material, enclosed in a mantle of the semiconductor material, is applied as anode.

9. A method according to any one or more of claims 1-12, where the electrolyte in which the anode has been placed, is equal to the electrolyte in which the cathode has been placed.

10. A method according to claim 9, where the electrolyte is a combination of NaCl and KCl, preferably a eutectic mixture of NaCl and KCl.

11. A method according to any one or more of the preceding claims, where a membrane is applied that is permeable to the one or more ionic compounds that are formed in step b), the membrane being present between the electrolyte in which the anode is placed and the electrolyte in which the cathode is placed.

12. A method according to claim 11, where a ceramic membrane is applied as membrane.

13. A method according to any one or more of claims 9-11, where a capture electrode is applied which is connected to an external voltage source, the capture electrode having a potential that is equal to or higher than that of the cathode, where the capture electrode has been placed in the electrolyte between the anode and cathode.

14. A method according to any one or more of claims 2-13, where in step b) additionally one or more compounds according to formula I are added.

15. A method according to any one or more of the preceding claims, where the reduction is carried out at a temperature of at least 400 °C, preferably at least 470 °C.

16. A method according to any one or more of claims 1-15, where an external voltage source is applied to apply a difference of potential between the anode and the cathode, the difference of potential being selected between 0.01 V and the standard reduction potential of the electrolyte.

17. A method according to any one or more of claims 9-16, where the electrolyte is forced to flow from the cathode to the anode and vice versa.

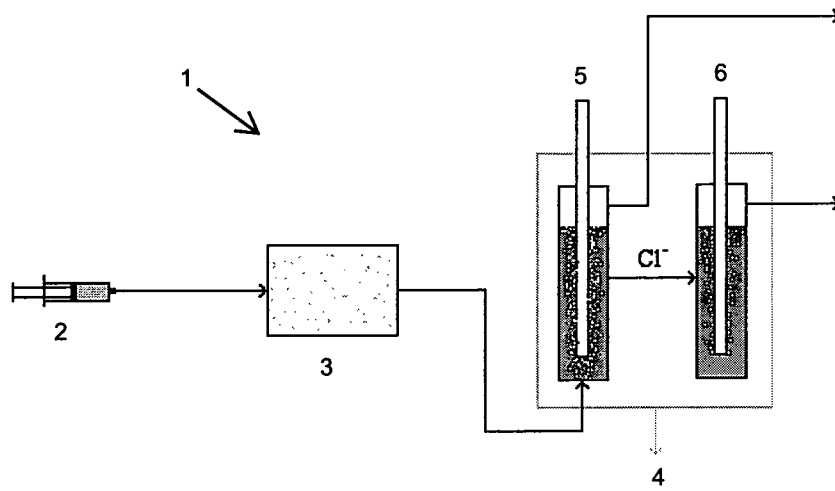


Fig. 1

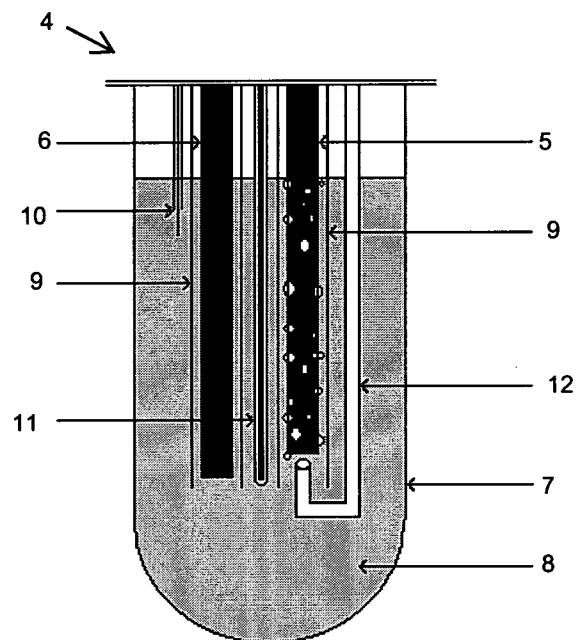


Fig. 2

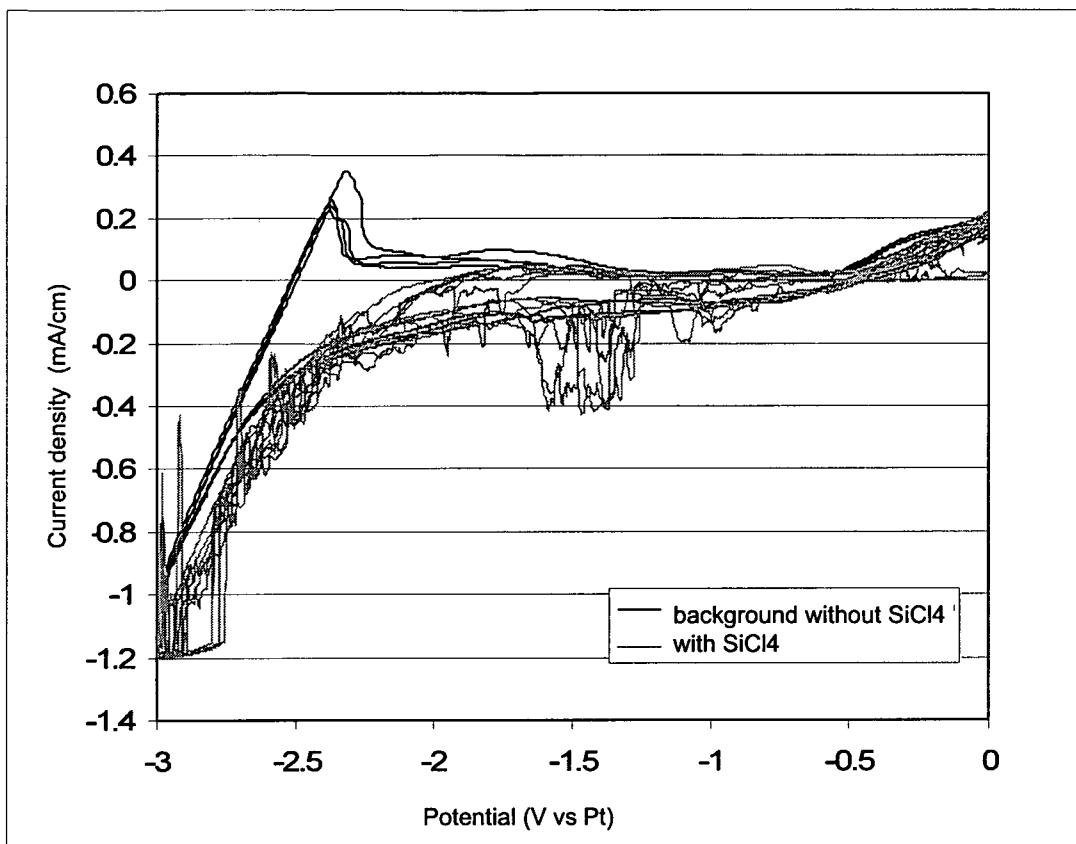


Fig. 3

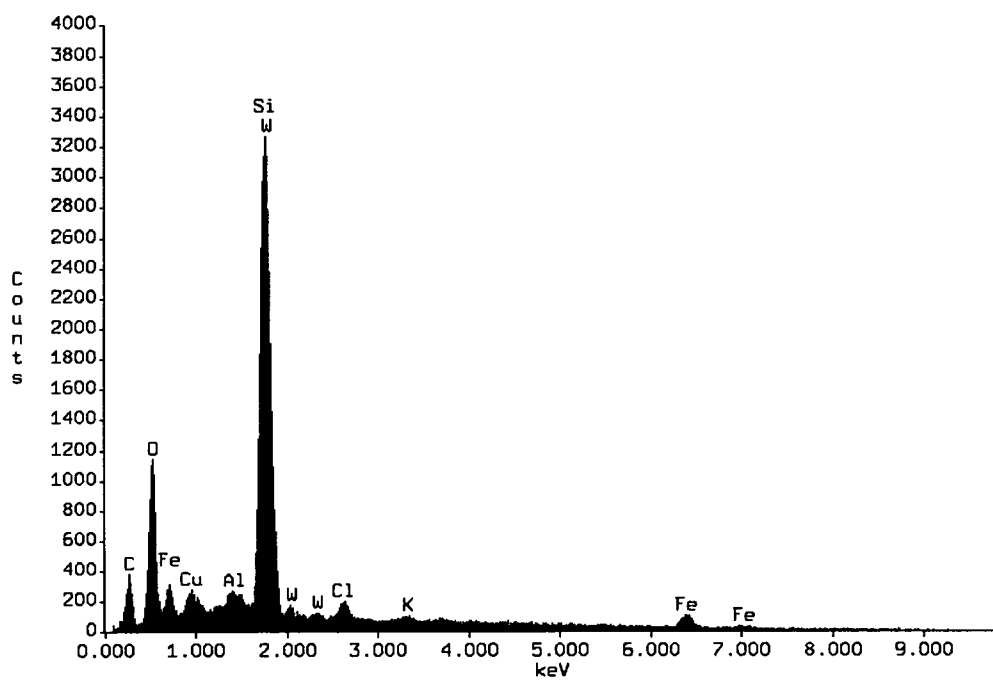
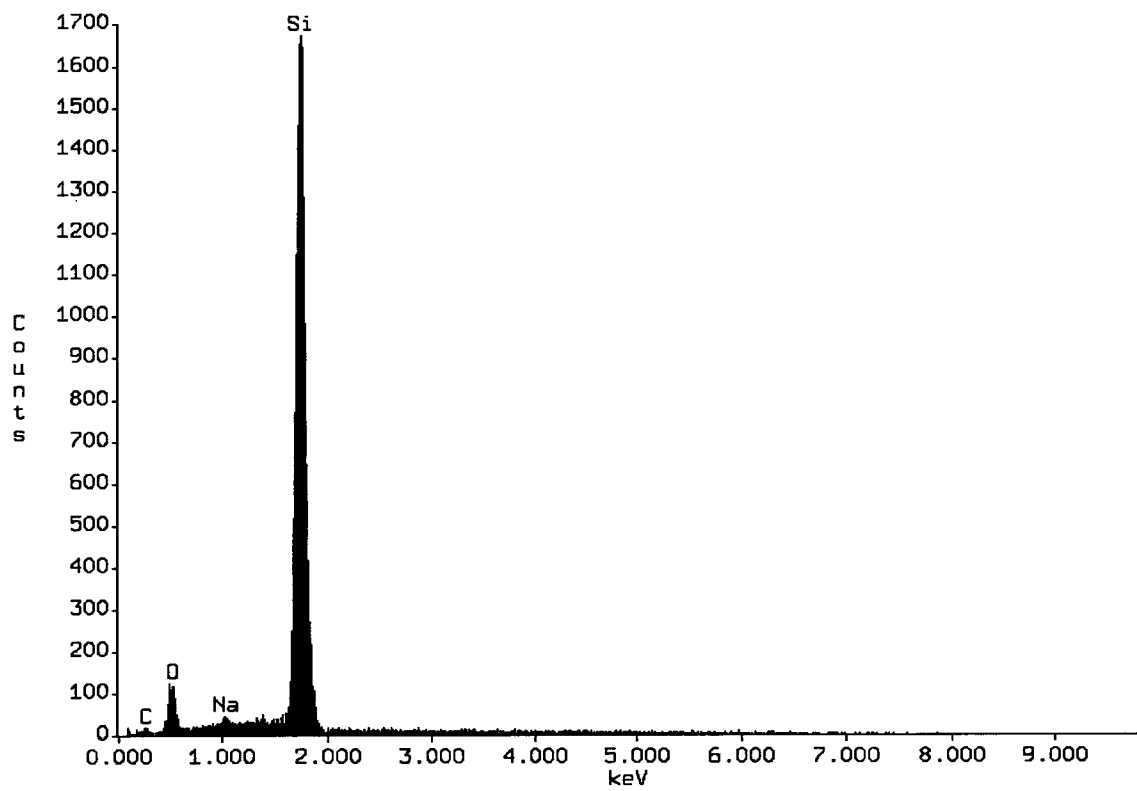


Fig. 4

**Fig. 5**