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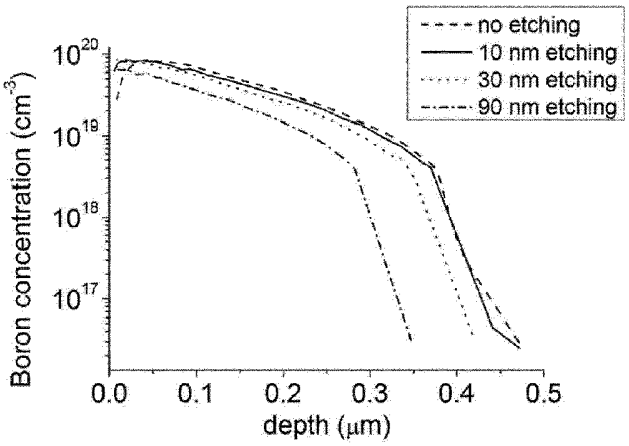
(54) **Surface boron doped layer of crystalline silicon solar cell with improved surface passivation.**

(57) Method of manufacturing a crystalline silicon solar cell, comprising providing a crystalline silicon substrate, and providing a boron doped surface layer in the crystalline silicon substrate with a peak boron doping concentration higher than 8E19cm^{-3}. The method further comprises removing a surface part of the boron doped layer and forming a passivation film on the boron doping layer. This results in a surface boron concentration just beneath the passivation film that is higher than 5E19cm^{-3}.



Surface boron doped layer of crystalline silicon solar cell with improved surface passivation

Field of the invention

The present invention relates to a method of manufacturing a crystalline silicon solar cell, comprising providing a crystalline silicon substrate, and providing a boron doped surface layer in the crystalline silicon substrate.

Prior art

International patent application WO2008/039067 discloses a method of manufacturing crystalline silicon solar cells with improved surface passivation. In the manufacturing method disclosed herein, a silicon oxide film with boron is removed using hydrogen fluoride (HF), and the surface is chemically oxidized using a HNO_3-based solution (as an exemplary implementation), resulting in 1-2nm of a silicon oxide film. In this process flow, the surface boron concentration just beneath the silicon oxide film is about 2-3E19cm^{-3} with a peak boron concentration of 8E19cm^{-3} or higher than that. Furthermore a SiNx layer is deposited over the silicon oxide with a thickness of 80-100nm, e.g. using a plasma enhanced chemical vapour deposition (PECVD).

The article by M.A. Kessler et al, 'Charge carrier lifetime degradation in Cz silicon through the formation of a boron-rich layer during BBr_3 diffusion processes' published in Semiconductor Science and Technology, volume 25 (2010) 055001, mentions a boron diffusion process normally accompanies a generation of a so-called boron rich layer (BRL) where boron is highly precipitated at the interface of the boron diffusion source and the silicon substrate. The boron concentration in BRL is higher than 2E20 cm^{-3} and sometimes even higher than 1E21 cm^{-3}. This is supposed to be caused by several physical phenomena. Most of the cases, the boron diffusion source is made of borosilicate glass (BSG) which is a mixed matrix of SiO_2:B_2O_3. At the temperature for boron diffusion, a red-ox reaction below takes place at the interface of BSG and the silicon substrate:

$$2\ B_2O_3 + 3\ Si \rightarrow 4\ B + 3\ SiO_2.$$

On the other hand, the solid solubility limit of boron in silicon is lower than 1.5E20 at lower than 1000°C, therefore the generation speed of elemental boron far exceeds the accepting speed of boron into the silicon substrate. Thus the generated

elemental boron is highly precipitated at the interface of BSG and the silicon substrate, with creating compound of silicon borate which is typically SiB_4 or SiB_6. When the diffusion source is elemental boron film which is usually amorphous boron, the creation of silicon borate and the formation of BRL also take place even more extremely. The BRL cannot be removed by HF solution. The surface passivation quality of the BRL is very poor; therefore the layer has to be removed to achieve a solar cell with a decent device performance.

The article by R. Müller et al, 'Evaluation of implantation annealing for highly-doped selective boron emitters suitable for screen-printed contacts' published in Solar Energy Materials & Solar Cells, vol 120A, January 2014, pages 431-435, discloses a method to form a surface boron-doped layer on a silicon substrate by boron ion implantation and a subsequent thermal annealing to recover the crystal structure which was damaged by ion implantation. The article also suggests a generation of BRL in this process flow when the annealing is carried out in an inert gas ambient and the peak concentration after the annealing results in higher than 8E19 cm^{-3}.

The article by A.H.G. Vlooswijk et al, 'Boron processing in solar cell industry: Boron diffusion in silicon wafers' in Chapter 16 of the book 'Boron: Compounds, Production and Application', Nova Science Publishers, 2010, discloses conventional processing of boron diffusion in silicon wafers. Thermal diffusion of boron using BSG as the diffusion source is described into a silicon substrate. An oxidation step during the cooling down from the diffusion temperature to the room temperature is applied which oxidizes the BRL completely and enables removal of the oxidized BRL together with the BSG by 1-step wet chemical etching by an HF solution. This oxidation step can be implemented using the thermal budget of the prior boron diffusion process and the extra process cost can be significantly limited. However, this oxidation step causes boron depletion on the surface of the boron doped layer where the surface boron concentration is less than half of the peak concentration as shown in Fig. 1, because boron is strongly segregated in SiO_2 at the BSG/Si interface even though the oxidation temperature is much lower than the temperature for the boron diffusion.

The article by L. Shen et al, 'A wet-chemical etching method to remove the boron-rich layer for n-type silicon solar cells', presented at 23rd International Photovoltaic Science and Engineering Conference (PVSEC-23), Taipei, Taiwan, 28th Oct-1st Nov 2013, discloses chemical etching of the BRL.

Summary of the invention

The present invention seeks to provide a manufacturing method for a crystalline silicon solar cell, wherein a boron doped layer is provided with a high boron concentration throughout the boron doped layer, including the surface layer.

According to the present invention, a method according to the preamble defined above is provided, wherein the boron doped surface layer has a peak boron doping concentration higher than $8E19cm^{-3}$, and the method further comprises removing a surface part of the boron doped layer, and the method further comprises forming a passivation film on the boron doping layer, resulting in a surface boron doping concentration just beneath the passivation film higher than $5E19cm^{-3}$. The passivation film is e.g. a thin silicon oxide film, formedby soaking the crystalline silicon substrate in a chemical solution.

This results in an improvements of the device output of such solar cell, yet only adds one simple, easy to implement and cost-efficient processing step. The improved surface passivation effect was unexpected as removal of the surface depletion layer leads to a higher boron surface concentration. Conventionally it is assumed that this increases the defect density at the surface, and therefore results in a poorer surface passivation. However, this conventional assumption does not take into account the more favorable (lower) surface concentration of minority carriers that can be achieved with a higher surface doping. In addition, the inventors identify a mechanism that crystal vacant sites are created in the surface boron depletion layer which appears in most of the conventional boron doping process. The invention embodiments, as described below in more detail, and in the appended claims, allow to take full advantage of this favorable effect while minimizing or even reducing the negative effects of the defect density and the crystal vacant sites. The solar cell performance is improved with only adding one step of wet chemical etching at room temperature within a series of other wet chemical process. Solar cell efficiency thus increases with minimum extra cost.

In a further aspect, the present invention also relates to an intermediate surface configuration of a crystalline silicon substrate, wherein the top layer of the crystalline silicon substrate is obtained using the method according to any one of the present invention embodiments. Furthermore, the present invention also relates to a crystalline

solar cell produced using the method according to any one of the present invention embodiments.

Short description of drawings

The present invention will be discussed in more detail below, using a number of exemplary embodiments, with reference to the attached drawings, in which

Fig. 1 shows a typical doping profile of a boron doped layer including BSG as the boron doping source in a crystalline silicon solar cell;

Fig. 2 shows a doping profile near the surface layer of a crystalline solar cell provided according to one of the invention embodiments; and

Fig. 3 shows a graph of open circuit voltage distribution as function of the etching depth of comparative samples manufactured; and

Fig. 4 shows a graph of minority carrier lifetime distribution as function of the etching depth of comparative samples manufactured; and

Fig. 5 shows a an example of a surface boron doping profile after phosphorus diffusion process using a diffusion barrier film on the boron-doped surface. .

Detailed description of exemplary embodiments

Solar cells made of single- or multi-crystalline silicon are usually provided with a dielectric coating on a front side (i.e. the light incident side) in order to lead the incident light effectively to the semiconductor layer. Such a dielectric coating is often referred to as anti-reflection coating (ARC) film.

The performance of a solar cell is largely influenced by the degree of suppression of recombination of the photo-generated carriers at the interface between the semiconductor layer and the ARC film. Suppression of recombination of the photo-generated carriers is normally realized using what is called surface passivation.

As an ARC film for crystalline silicon solar cell with a phosphorus-doped layer on the top side of the cell, a silicon nitride film is often used because it has a good anti-reflecting effect and a sufficient surface passivation effect can be expected.

One of the factors currently limiting the output of c-Si solar cells is the surface recombination at highly-doped boron layers. Such layers are essential in most new types of c-Si solar cells, either as an emitter or as a Back Surface Field (BSF). When the layer is used as an emitter, n-type wafers can be easily applied which is potentially

more appropriate for high-performance solar cell than widely used p-type wafers whose quality is reported to be degraded by light irradiance. When the layer is used as a BSF, it can substitute widely used aluminium paste BSF, resulting in larger photo-generated carriers by enhancing rear side internal reflection. The highly-doped boron layers also enable a bifacial structure by combining a phosphorus-doped layer on the other side, which can collect light from both sides with the advantage of larger daily yield considering the Sun is moving while solar cells are normally fixed. For the boron-doped layer, surface passivation effect of a silicon nitride film is very poor. Either of thin thermal silicon oxide, thin chemical silicon oxide, or atomic-layer-deposited (ALD) aluminium oxide layer is used for the surface passivation with silicon nitride above to enhance anti-reflection effect.

Fig. 1 shows a typical boron doping profile of BSG (borosilicate glass, the boron doping source for thermal diffusion) and the emitter surface, after the oxidation step which enables removal of the diffusion source by wet chemical etching using HF solution. Boron is strongly segregated toward BSG near the interface between BSG and silicon. The oxidation temperature is more than 100°C lower than the diffusion temperature. Even at such low temperature which enables complete oxidation of BRL, boron atoms are extracted from silicon towards BSG as seen above. If no oxidation is carried out, boron depletion does not take place. But BRL at the BSG/Si interface is quite tough to remove.

Figs. 2, 3 and 4 show characteristics (boron concentration as function of depth into boron doped layer, open circuit voltage distribution as function of the sample etching depth, and minority carrier lifetime distribution as function of the sample etching depth, respectively) of a substrate processed according to an embodiment of the present invention. A boron doped layer with a boron depletion layer of 30 – 40 nm is formed on a surface textured silicon wafer by boron diffusion with BBr_3 system including BRL oxidation step. Four groups are prepared and the surface of each group is etched except the reference group. The boron depletion layer is removed partly (10 nm deep), almost completely (30 nm deep), and over-etched (90 nm). Thus, the surface part of the boron doped layer which is removed may include the boron depletion layer, or may be part of the boron depletion layer. After the surface etching, a chemical oxide is formed on the surface by HNO_3-based solution under 100°C including the reference (no etching) group, and PECVD SiNx is deposited above the chemical oxide. Solar

cells are made using this structure as the front side emitter of n-type silicon substrate and the device performance was measured. The trends of both the open circuit voltage and the minority carrier lifetime indicate the effect of the surface etching clearly, which suggest the effect of this invention.

Highly-doped boron layers formed by processes used in the PV industry often have a so-called surface depletion region, i.e. in a very thin surface layer (up to about 20 - 100 nm, depends on the formation method) the boron concentration is less than the peak concentration. Recent experimental results and theoretical analysis suggest that removal of this layer reduces the surface recombination. This would lead to improvement of 0.5% abs in the efficiency of the solar cell.

Fig. 3 shows one of the experimental results in which the average open circuit voltage is improved from 662 mV to 682 mV by etching 90 nm of the surface. The boron doping profiles of these solar cells are shown in Fig. 2. Even by just etching 10 nm where the boron depletion layer is not completely removed, the average open circuit voltage is improved to 672 mV. Thus the advantageous effects of the present invention are achieved when the surface part forms only a part of the boron doped layer (in the case the etching amount is thinner than the boron depletion layer), or when the surface part includes a boron depletion layer (in the case the etching amount is as thick as or thicker than the boron depletion layer). The effect is most apparent when the boron depletion layer has a surface boron concentration less than half of the peak boron concentration of the boron doped layer.

Fig. 4 shows another example of the experimental results in which the average minority carrier lifetime is improved from 280 μs to 530 μs by etching 90 nm of the surface. The samples have $p^+/n/p^+$ symmetric structure on both sides textured wafers, and the p^+-layers of both sides formed by BBr_3 diffusion are covered with a passivation film oxidized chemically by soaking the sample in HNO_3 solution. All the etched surfaces of 10, 30, and 90 nm just before the chemical oxidation process were hydrophilic, or wettable by water, while that of no etching was hydrophobic. Moreover, SiNx film is deposited on the silicon oxide using PECVD. The same structure as this passivation film is formed on the solar cell samples for Fig. 3, which proves it is feasible to apply the passivation film comprising thin silicon oxide formed by soaking in chemical solution on etched surfaces, resulting in minority carrier lifetime long enough to demonstrate the high performance of solar cell devices.

To achieve this desired effect, the present invention in a first embodiment comprises a method of manufacturing a crystalline silicon solar cell, comprising providing a crystalline silicon substrate, providing a boron doped surface layer in the crystalline silicon substrate with a (peak) boron doping concentration higher than $8E19cm^{-3}$; removing a surface part of the boron doped layer, and forming a passivation film on the boron doping.

It is noted that the surface of the crystalline silicon substrate may be textured before the process to form the boron doped surface layer.

Providing the boron doped surface layer in the crystalline silicon substrate may be formed using boron ion implantation followed by thermal annealing (e.g. at a temperature higher than 920°C) to activate the boron as an acceptor dopant. The ambient environment during the thermal annealing step may be an inert gas ambient, or it may comprise oxygen (O_2), or other constituents which can thermally oxidize the silicon surface, such as oxidizing gas either of O_2, H_2O, O_3, CO_2, or N_2O.

Alternatively, the boron doped surface layer is provided using thermal diffusion of boron into the crystalline silicon substrate. The diffusion process may be followed by thermal oxidation using O_2, H_2O, N_2O, CO_2, O_3, etc. The thermal oxidation is e.g. carried out at temperature higher than 500°C, e.g. higher than 600°C, more specifically higher than 700°C. The ambient of the thermal oxidation may contain an oxidizing gas of either O_2, H_2O, O_3, CO_2, or N_2O.

If the boron doped surface layer is obtained using thermal diffusion, the thermal oxidation may be carried out during the cooling down step after the thermal diffusion, allowing to use the heat then available. Alternatively, when the boron doped surface layer is obtained using ion implantation followed by thermal annealing, the thermal oxidation may similarly be carried out during the cooling down step after the thermal annealing. In both cases, the boron depletion layer will form during the process.

In an embodiment of the present invention, the boron doped surface layer is obtained using boron ion implantation or thermal diffusion, e.g. using borosilicate glass (BSG) and etching of the BSG layer after annealing (thermal diffusion), e.g. using wet chemical etching such as HF etching.

In a further embodiment, the removed surface part of the boron doped layer is between 5 and 200 nm thick, which is sufficient to remove the disadvantageous effect of the boron depletion layer. In further embodiments, a sufficient effect is already

achieved after removing between 5 and 100 nm of the surface of the boron doped layer. Removing the boron depletion layer part is obtained in a further embodiment by etching, e.g. using wet chemical etching (acid or alkali) or plasma etching.

The etching process is carried out using any one of the solutions listed below:

Acid etching: NH_4F; NH_4F + HF; $NOHSO_4$ + HF; HNO_3 + HF; HNO_3 + HF + H_2SO_4; HNO_3 + HF + CH_3COOH; Cr_2O_3 (or Cr_2O_7)+ HF; $KMnO_4$ (or MnO_2) + HF; H_2O_2 + HF; O_3 + HF; H_3PO_4. Note that HF can be exchanged for other chemicals which contains HF, like NH_4F, NaF.

Alkali etching: NaOH; KOH; TMAH; Na_2CO_3.

It is noted that the boron doped surface layer is an emitter layer in a silicon solar cell, but the present invention embodiments can also be applied as a back (or front) surface field layer in a silicon solar cell.

By etching this boron depleted layer, a higher surface concentration can be realized, resulting in a highly boron doped layer on the surface of a crystalline silicon solar cell (emitter side, but BSF is also applicable) whose surface concentration is larger than $5E19cm^{-3}$ and peak concentration is larger than $8E19cm^{-3}$. Thus, the step of removing is applied until a surface concentration of boron is higher than $5E19cm^{-3}$. This is accomplished without significant increase of the sheet resistance, resulting in an improvement of surface passivation and device performance. When the surface with this highly-doped boron is exposed, the surface may show a hydrophilic behaviour, or that is, wettable by water. This feature is also supposed to be that of the BRL surface, and different from normal silicon surface after HF treatment which is hydrophobic. The surface with the boron depletion layer after BSG removal is also hydrophobic.

Subsequently, a passivation film is formed on the etched surface. In an embodiment, the passivation film is a thin silicon oxide film by soaking the crystalline silicon substrate in chemical solution. Chemical oxidation (e.g. nitric acid process) at temperature lower than 150°C is also important because it does not cause surface boron depletion while it provides a good surface passivating film and stabilizes the atomic bond status at the exposed surface. The surface with the thin chemical oxide is hydrophilic.

In another embodiment, the passivation film is an aluminium oxide (Al_2O_3) film. It is more favourable when Al_2O_3 is formed by atomic layer deposition (ALD). The

temperature for ALD-Al_2O_3 is normally about 200°C and hardly higher than 400°C, which does not cause surface boron depletion, either.

In a further embodiment a sheet resistance of the boron doped surface layer after removing the surface part of the boron doped layer is less than 300 Ω/sq, e.g. less than 150Ω/sq, more specifically lower than 100 Ω/sq.

When a boron heavily doped layer is formed with a thermal process, the peak concentration is close to its solid solubility limit (1-1.5E20 /cm^3) and normally higher than 8E19. If the thermal process in the manufacturing method involves thermal oxidation, a silicon oxide film is formed on the surface of the (boron) doped layer. Because the solid solubility limit of boron in silicon oxide is much higher than that in silicon and boron atoms are strongly segregated at the interface between silicon oxide and silicon as shown in Fig. 1, boron atoms near the surface in the boron doped layer are attracted toward the silicon oxide at the oxidation temperature which is normally lower than that for boron doping, resulting in a lower surface concentration at the surface than the peak concentration. This surface boron depletion causes poorer surface passivation.

Another unfavourable effect of boron depletion is that it creates vacant sites in the crystal lattice of silicon. Because the doped boron atoms near the BSG/Si interface are segregated toward BSG at low temperature within short time, silicon atoms around the vacant sites where boron atoms used to be do not have enough time and/or thermal migration energy to re-fill the sites. These vacant sites behave as crystal defects which cause minority carrier recombination, resulting in poorer solar cell performance. Therefore, etching the boron depleted layer has a function of removing such layer including vacant sites in the crystal lattice. The boron segregation toward BSG at low temperature even influences on the layer deeper than where boron depletion is observed, therefore etching deeper than the boron depleted layer is effective for solar cell performance in some cases.

In case that the oxidation step using thermal annealing or thermal oxidation is not carried out in the forming process of the highly boron doped layer, boron is heavily precipitated (larger than 2E20cm^{-3}) at the surface of the doped layer, which is called a boron-rich layer or BRL. Thus, the surface part of the boron doped layer comprises a boron rich layer, e.g. having a boron concentration larger than 2E20cm^{-3}. The BRL is known to make the surface passivation very poor and is difficult to remove by a simple

chemical process. In a known, conventional process, this BRL is oxidized with a process like thermal annealing or thermal oxidation, or diluted into a deposited silicon oxide film with subsequent thermal annealing, and chemically removed subsequently, similar to removing a BSG layer as described above. The BRL may be removed using a similar processing step as the removal of the boron depletion layer as described above.

It is noted that with the state-of-the-art production of highly boron doped layers, boron depletion near the surface cannot be avoided. The physics can be explained as below:

During the thermal diffusion process, boron atoms precipitate between the diffusion source and the emitter and form a several nm thick boron rich layer (BRL). As described above, because it is bad for surface passivation and hard to remove by chemical process as it is, it is usually oxidized thermally during the cooling down step from the boron diffusion temperature to the room temperature for easier removal together with the BSG by subsequent HF treatment. The oxide formed on the emitter surface in this step has enough capacity to locate boron atoms in it, and attracts boron atoms near the surface in the emitter. This causes boron atom depletion near the surface in the emitter, that is, the boron concentration of the surface becomes lower than the peak boron concentration at a certain depth as shown in Fig. 1.

In a certain process flow to make a solar cell, phosphorus highly-doped layer is formed; before or after the boron emitter is formed; on the other side of the substrate or the patterned area where boron doped layer is not formed; by phosphorus diffusion or phosphorus ion implantation followed by thermal annealing. This is e.g. implemented in a further embodiment of the present invention as a processing step following the step of providing the boron doped layer, using application of a (possibly patterned) coating of silicon oxide film on top of the boron doped surface layer, and phosphorous diffusion to the area where no coating is present.

In an embodiment, the formation of the phosphorus-doped layer is obtained by a thermal process either of thermal diffusion or ion implantation followed by thermal annealing. The step to form the phosphorus doped layer is carried out before the surface part of the boron doped layer is removed in a further embodiment. The thermal diffusion of phosphorus can even be carried out before the boron doped layer is obtained.

In a further embodiment, the thermal diffusion of phosphorus is carried out after the boron doped layer is obtained with a diffusion barrier formed on the surface of the boron doped layer. It is noted that this specific step would also cause boron depletion, the effect of which is overcome by applying the method according to any of the embodiments described herein. Furthermore, the diffusion barrier may be removed before the surface part of the boron doped layer is removed. The diffusion barrier may comprise a silicon oxide film formed by either of thermal oxidation, chemical vapor deposition, or coating and baking of a silanol [$(SiHOH)_nH_2$]-based liquid.

A diffusion barrier is deposited on the boron emitter to prevent over diffusion of phosphorus, but the barrier material attracts boron atoms on the emitter surface because practically working material at this moment is only silicon oxide. This also causes boron surface depletion, or may even enhance the boron surface depletion. Fig. 5 shows an example of a surface boron doping profile after phosphorus diffusion process using a diffusion barrier film on the boron-doped surface. In this case, boron is depleted as deeply as 100 nm. Presuming from the example of Figs 2 and 3 where boron depletion layer is about 30 – 40 nm deep and the effect of etching 90 nm is identified, a negative impact of boron depletion can be also double of the boron depletion layer, that is, about 200 nm.

Damage recovery anneal of boron ion implanted wafers for solar cell process can be more effective when it is carried out under a slightly oxygen comprising atmosphere. While phosphorus diffusion incorporates a lot of inactive phosphorus into highly dope layer, boron diffusion does not allow inactive boron. Therefore perfect activation is necessary for ion implantation to compete with diffusion process in case of boron. But thermal substitution of interstitial boron into a crystal lattice site is much more challenging because a boron atom is one third lighter than a silicon atom. A simple way to remove such excess inactive boron atoms is to extract them by making an oxide film on the surface. On the other hand, surface boron depletion also takes place as the side effect of this with even making crystal vacant sites because the extraction of boron atoms near the surface is often faster and/or with lower migration energy than the surrounding silicon atoms re-filling the vacant sites.

The boron depletion layer on the surface (= the surface boron concentration is lower than the peak concentration) is removed (or reduced), by a simple etching method (wet chemical or plasma). This results in improving surface passivation.

In an embodiment, the state-of-the-art manufacturing as described in the prior art document WO2008/039067 could be modified by adding this step, e.g. after the removal of the boron containing silicon oxide film and before the chemical oxidation e.g. by HNO_3 treatment. Thus, in a further embodiment, after removing the boron depletion layer part, the boron doped surface layer is coated with a chemical oxide layer, also referred to as nitric acid oxidation of silicon (NAOS).

In a further embodiment, the thin silicon oxide is between 0.5-10 nm thick, e.g. between 0.5-5 nm thick, more specifically about 1-2 nm thick. The temperature of the chemical solution to form the thin silicon oxide on the boron doped layer is under 150°C, e.g. at room temperature.

A further layer is applied in a further embodiment, the further layer comprising aluminum oxide (Al_2O_3). It may be formed by atomic layer deposition (ALD). This can be applied on top of the chemical oxide layer which enhance the passivation effect of the thin chemical oxide layer.

In another embodiment, an Al_2O_3 film can be formed directly on the boron doped layer after the surface part is removed, to directly passivate the surface. It may also be formed by ALD.

As in many other manufacturing methods for solar cells, at the end of the process an anti-reflective coating layer is applied. In a further embodiment of the present invention, a further layer is applied to achieve that effect, the further layer comprising a dielectric film, e.g. a silicon nitride film in combination with hydrogen.

The improved surface passivation effect was unexpected as removal of the surface depletion layer leads to a higher boron surface concentration. Conventionally it is assumed that this increases the defect density at the surface, and therefore results in a poorer surface passivation. However, this conventional concept does not take into account the more favourable (lower) surface concentration of minority carriers that can be achieved with a higher surface doping. The invention allows to take full advantage of this favourable effect while minimizing or even reducing the negative effects of the defect density.

Furthermore, a mechanism is identified that crystal vacant sites are created in the surface boron depletion layer. The effect of the invention enables the removal of this unfavourable layer including crystal vacant sites caused by boron depletion, and leads to improved solar cell performance.

Moreover, the boron doping profile is kept after the subsequent process of forming the passivation film without inducing surface boron depletion. It is effective to apply a passivation film even on a hydrophilic crystalline silicon surface when a surface part of a boron doped layer is removed, while a hydrophobic surface was supposed to be always necessary to effectively apply a passivation film.

It was thus found that the device output of a solar cell can be improved when the layer with boron surface depletion of a highly boron doped layer in the device is partially or completely removed. To achieve this cheap and efficient methods can be used. The method embodiments described herein may be advantageously used in every silicon substrate manufacturing method wherein a boron doped layer is used, and the present invention this also relates to an intermediate surface configuration of a crystalline silicon substrate, wherein the top layer of the crystalline silicon substrate is obtained using the method according to any one of the embodiments described above, as well as to a crystalline solar cell produced using the method according to any one of the present invention embodiments.

The present invention can be described as one of many embodiments as follows:

Embodiment 1. Method of manufacturing a crystalline silicon solar cell, comprising

providing a crystalline silicon substrate,

providing a boron doped surface layer in the crystalline silicon substrate with a peak boron doping concentration higher than 8E19cm^{-3}; and

removing a surface part of the boron doped layer;

and forming a passivation film on the boron doped layer;

resulting in a surface boron concentration just beneath the passivation film that is higher than 5E19cm^{-3}.

Embodiment 2. Method according to embodiment 1, wherein the removed surface part of the boron doped layer is between 5-200 nm thick.

Embodiment 3. Method according to embodiment 1 or 2, wherein the boron doped surface layer is obtained using boron ion implantation or thermal diffusion.

Embodiment 4. Method according to any one of embodiments 1-3, wherein the obtaining step of the boron doped surface layer is followed by thermal oxidation.

Embodiment 5. Method according to any one of embodiments 1-3, wherein the surface part includes a boron rich layer, e.g. having a boron concentration higher than 2E20 cm^{-3}.

Embodiment 6. Method according to any one of embodiments 1-5, wherein removing the surface part of the boron doped layer is obtained by etching, e.g. using wet chemical etching or plasma etching.

Embodiment 7. Method according to any one of embodiments 1-6, wherein a sheet resistance of the boron doped surface layer after removing the surface part of the boron doped layer is less than 300Ω/sq.

Embodiment 8. Method according to any one of embodiments 1-7, wherein the passivation film is a thin silicon oxide film by soaking the crystalline silicon substrate in chemical solution.

Embodiment 9. Method according to embodiment 8, the thin silicon oxide film is between 0.5-10 nm thick, e.g. between 0.5-5 nm thick.

Embodiment 10. Method according to embodiment 8 or 9, wherein the temperature of the chemical solution to form the thin silicon oxide on the boron doped layer is under 150°C, e.g. at room temperature.

Embodiment 11. Method according to any one of embodiments 8-10, wherein a further layer is applied on the chemically oxidized thin silicon oxide, the further layer comprising aluminum oxide (Al_2O_3) film.

Embodiment 12. Method according to any one of embodiments 1-7, wherein the passivation film is an aluminum oxide (Al_2O_3) film.

Embodiment 13. Method according to embodiment 11 or 12, the aluminum oxide film is formed by atomic layer deposition.

Embodiment 14. Method according to any one of embodiments 1-13, wherein the boron doped surface layer is an emitter layer in a silicon solar cell.

Embodiment 15. Method according to any one of embodiments 1-13, wherein the boron doped surface layer is a back or front surface field layer in a silicon solar cell.

Embodiment 16. Method according to any one of embodiments 1-15, comprising the step of forming a phosphorous doped layer to the area where no surface boron doped layer is present.

Embodiment 17. Method according to any one of embodiments 1-16, wherein a further layer is applied, the further layer comprising a dielectric film, e.g. a silicon nitride film in combination with hydrogen.

Embodiment 18. Method according to any one of embodiments 1-17, wherein the surface of the crystalline silicon substrate is textured before the process to form the boron doped surface layer.

Embodiment 19. An intermediate surface configuration of a crystalline silicon substrate, wherein the top layer of the crystalline silicon substrate is obtained using the method according to any one of embodiments 1-18.

Embodiment 20. Crystalline silicon solar cell produced using the method according to any one of embodiments 1-18.

Various embodiments of the present invention have been described above, and may be applied in combination where applicable. Furthermore, modifications and alternative implementations of some parts or elements are possible, and are included in the scope of protection as defined in the appended claims.

CONCLUSIES

1. Werkwijze voor het vervaardigen van een kristallijne silicium zonnecel, omvattende
verschaffen van een kristallijn siliciumsubstraat,
verschaffen van een met boor gedoteerde oppervlaktelaag in het kristallijn siliciumsubstraat met een piekboordoteringsconcentratie die hoger is dan $8E19cm^{-3}$; en
verwijderen van een oppervlaktedeel van de met boor gedoteerde laag;
en vormen van een passiveringsfilm op de met boor gedoteerde laag;
resulterend in een oppervlakteboorconcentratie direct onder de passiveringsfilm die hoger is dan $5E19cm^{-3}$.

2. Werkwijze volgens conclusie 1, waarbij het verwijderde oppervlaktedeel van de met boor gedoteerde laag tussen 5-200 nm dik is.

3. Werkwijze volgens conclusie 1 or 2, waarbij de met boor gedoteerde oppervlaktelaag verkregen is met boorionenimplantatie of met thermische diffusiie.

4. Werkwijze volgens één van de conclusies 1-3, waarbij de stap van verkrijgen van de met boor gedoteerde oppervlaktelaag wordt gevolgd door thermische oxidatie.

5. Werkwijze volgens één van de conclusies 1-3, waarbij het oppervlaktedeel een rijke boorlaag omvat, bijvoorbeeld met een boorconcentratie die hoger is dan $2E20cm^{-3}$.

6. Werkwijze volgens één van de conclusies 1-5, waarbij verwijderen van het oppervlaktedeel van de met boor gedoteerde laag wordt verkregen door etsen, bijvoorbeeld met gebruik van nat-chemisch etsen of plasmaetsen.

7. Werkwijze volgens één van de conclusies 1-6, waarbij een laagweerstand van de met boor gedoteerde oppervlaktelaag na verwijderen van het oppervlaktedeel van de met boor gedoteerde laag lager is dan $300\Omega/\square$.

8. Werkwijze volgens één van de conclusies 1-7, waarbij de passiveringsfilm een dunne siliciumoxidefilm is, verkregen door het dompelen van het kristallijn siliciumsubstraat in een chemische oplossing.

9. Werkwijze volgens conclusie 8, waarbij de dunne siliciumoxidefilm tussen 0.5-10 nm dik is, bijvoorbeeld tussen 0.5-5 nm.

10. Werkwijze volgens conclusie 8 of 9, waarbij de temperatuur van de chemische oplossing voor het vormen van de dunne siliciumoxide op de met boor gedoteerde laag onder 150°C ligt, bijvoorbeeld op kamertemperatuur.

11. Werkwijze volgens één van de conclusies 8-10, waarbij een verdere laag wordt aangebracht op de chemisch geöxideerde dunne siliciumoxide, waarbij de verdere laag een aluminiumoxide (Al_2O_3) film omvat.

12. Werkwijze volgens één van de conclusies 1-7, waarbij de passiveringsfilm een aluminiumoxide (Al_2O_3) film is.

13. Werkwijze volgens conclusie 11 of 12, waarbij de aluminiumoxide film wordt gevormd door atomische-laagdepositie.

14. Werkwijze volgens één van de conclusies 1-13, waarbij de met boor gedoteerde oppervlaktelaag een emitterlaag in een silicium zonnecel is.

15. Werkwijze volgens één van de conclusies 1-13, waarbij de met boor gedoteerde oppervlaktelaag een oppervlakteveldlaag aan de achterzijde of aan de voorzijde is in een silicium zonnecel.

16. Werkwijze volgens één van de conclusies 1-15, omvattende de stap van het vormen van een met fosfor gedoteerde laag op het gebied waar geen met boor gedoteerde laag aanwezig is.

17. Werkwijze volgens één van de conclusies 1-16, waarbij een verder laag wordt aangebracht, en de verdere laag een diëlektrische film omvat, bijvoorbeeld een siliciumnitirde film in combinatie met waterstof.

18. Werkwijze volgens één van de conclusies 1-17, waarbij het oppervlakte van het kristallijn siliciumsubstraat van een textur wordt voorzien voorafgaand aan het proces om de met boor gedoteerde oppervlaktelaag te vormen.

19. Een tussenliggende oppervlakteconfiguratie van een kristallijn siliciumsubstraat, waarbij de toplaag van het kristallijn siliciumsubstraat is verkregen met de werkwijze volgens één van de conclusies 1-18.

20. Kristallijne silicium zonnecel vervaardigd met gebruik van de werkwijze volgens één van de conclusies 1-18.

Fig. 1

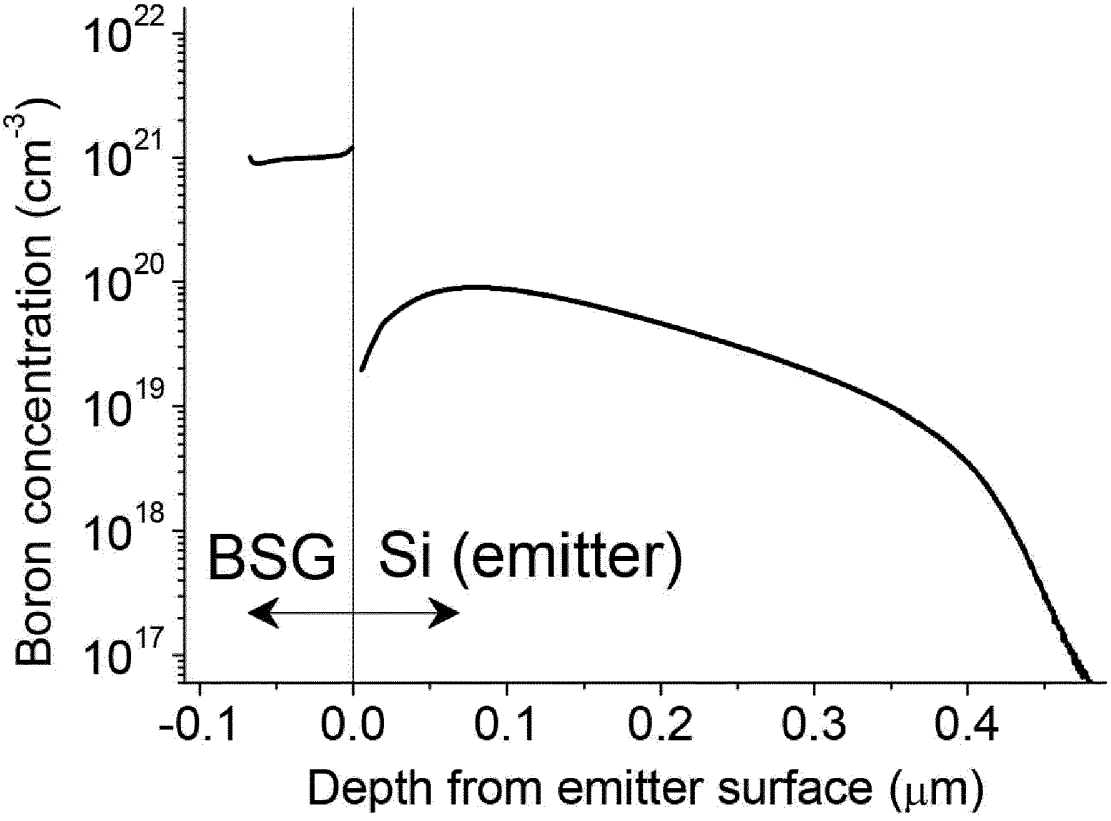

Boron concentration (cm-3)
10^22
10^21
10^20
10^19
10^18
10^17
BSG
Si (emitter)
-0.1
0.0
0.1
0.2
0.3
0.4
Depth from emitter surface (μm)

Fig. 2

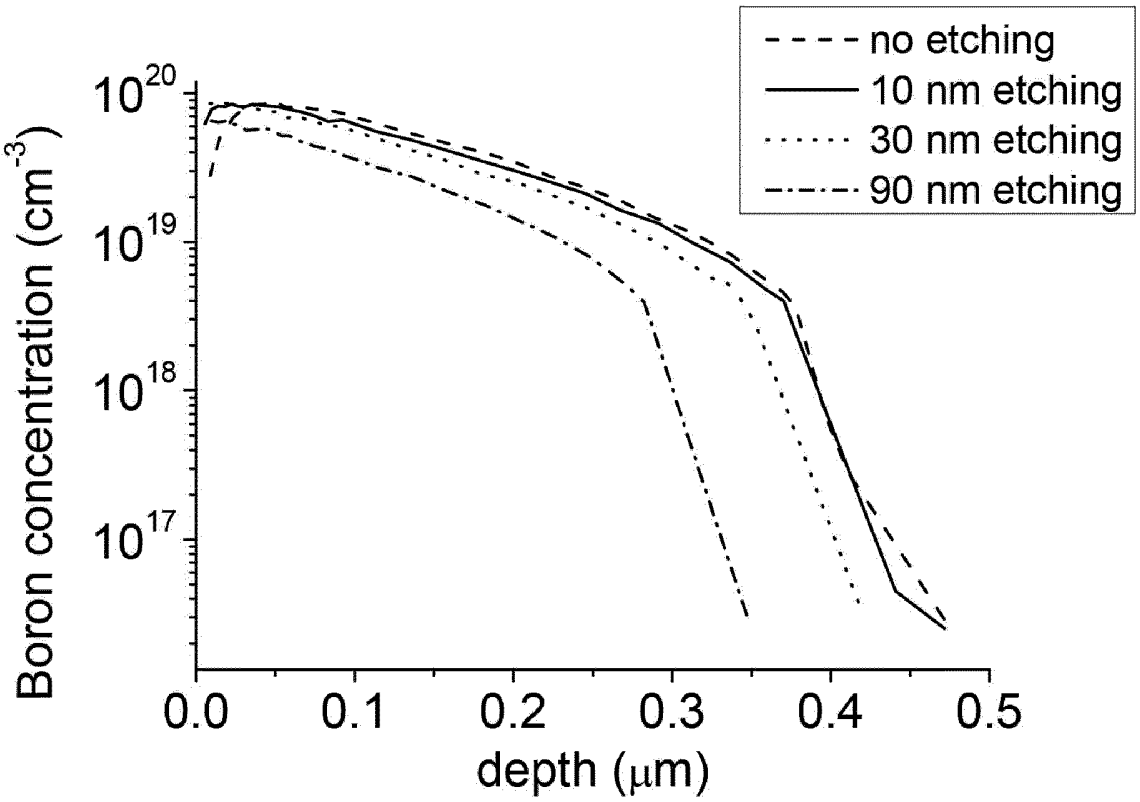

no etching
10 nm etching
30 nm etching
90 nm etching
Boron concentration (cm-3)
10^20
10^19
10^18
10^17
0.0
0.1
0.2
0.3
0.4
0.5
depth (μm)

Fig. 3

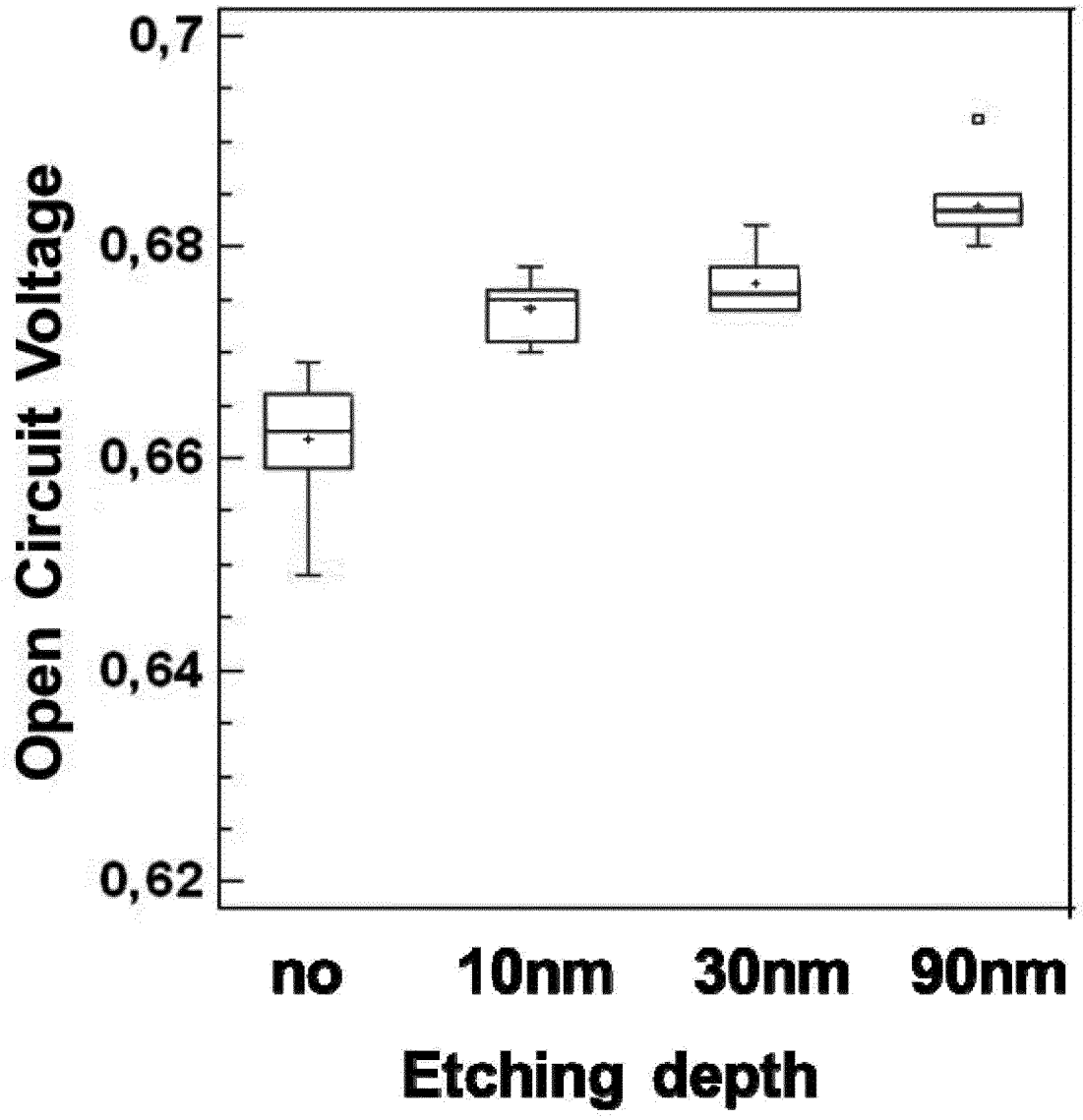

0,7
0,68
0,66
0,64
0,62
Open Circuit Voltage
no
10nm
30nm
90nm
Etching depth

Fig. 4

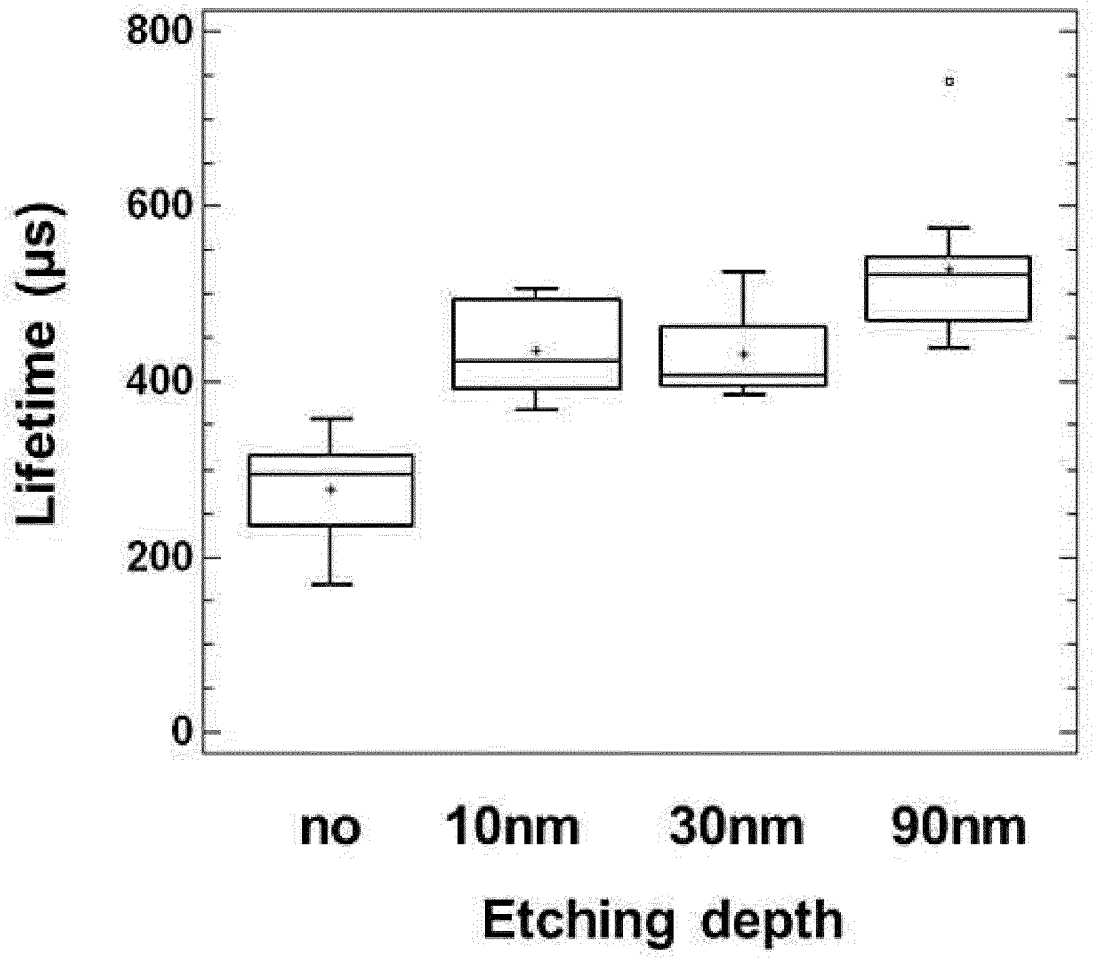
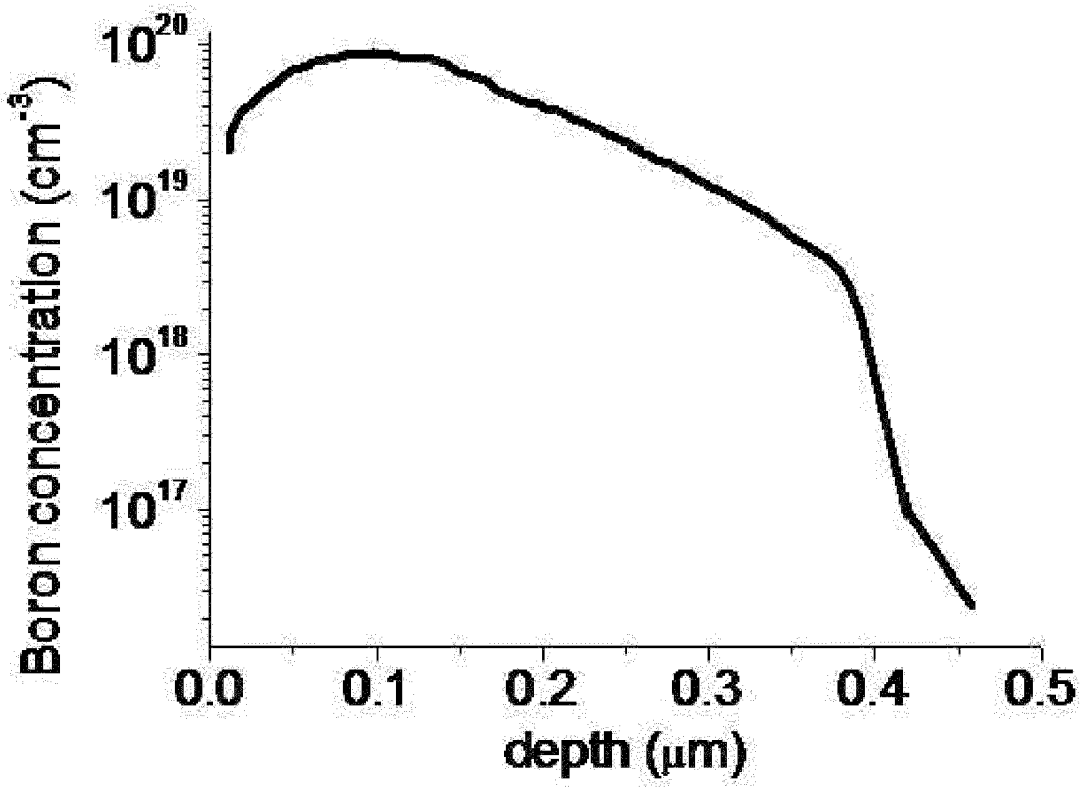


Fig. 5


Boron concentration (cm^{-3})
10^{20}
10^{19}
10^{18}
10^{17}
0.0
0.1
0.2
0.3
0.4
0.5
depth (μm)

SAMENWERKINGSVERDRAG (PCT)

RAPPORT BETREFFENDE NIEUWHEIDSONDERZOEK VAN INTERNATIONAAL TYPE

IDENTIFICATIE VAN DE NATIONALE AANVRAGE	KENMERK VAN DE AANVRAGER OF VAN DE GEMACHTIGDE
	P6049042NL
Nederlands aanvraag nr. **2012212**	Indieningsdatum **06-02-2014**
	Ingeroepen voorrangsdatum

Aanvrager (Naam)

Stichting Energieonderzoek Centrum Nederland

Datum van het verzoek voor een onderzoek van internationaal type	Door de Instantie voor Internationaal Onderzoek aan het verzoek voor een onderzoek van internationaal type toegekend nr.
03-05-2014	**SN 61937**

I. CLASSIFICATIE VAN HET ONDERWERP (bij toepassing van verschillende classificaties, alle classificatiesymbolen opgeven)

Volgens de internationale classificatie (IPC)

H01L31/0216 **H01L31/18**

II. ONDERZOCHTE GEBIEDEN VAN DE TECHNIEK

Onderzochte minimumdocumentatie

Classificatiesysteem	Classificatiesymbolen
IPC	**H01L**

Onderzochte andere documentatie dan de minimum documentatie, voor zover dergelijke documenten in de onderzochte gebieden zijn opgenomen

III.	☐ **GEEN ONDERZOEK MOGELIJK VOOR BEPAALDE CONCLUSIES**	(opmerkingen op aanvullingsblad)
IV.	☐ **GEBREK AAN EENHEID VAN UITVINDING**	(opmerkingen op aanvullingsblad)

ONDERZOEKSRAPPORT BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE

Nummer van het verzoek om een onderzoek naar de stand van de techniek
NL 2012212

A. CLASSIFICATIE VAN HET ONDERWERP
INV. H01L31/0216 H01L31/18
ADD.

Volgens de Internationale Classificatie van octrooien (IPC) of zowel volgens de nationale classificatie als volgens de IPC.

B. ONDERZOCHTE GEBIEDEN VAN DE TECHNIEK

Onderzochte miminum documentatie (classificatie gevolgd door classificatiesymbolen)
H01L

Onderzochte andere documentatie dan de mimimum documentatie, voor dergelijke documenten, voor zover dergelijke documenten in de onderzochte gebieden zijn opgenomen

Tijdens het onderzoek geraadpleegde elektronische gegevensbestanden (naam van de gegevensbestanden en, waar uitvoerbaar, gebruikte trefwoorden)
EPO-Internal, WPI Data, INSPEC

C. VAN BELANG GEACHTE DOCUMENTEN

Categorie °	Geciteerde documenten, eventueel met aanduiding van speciaal van belang zijnde passages	Van belang voor conclusie nr.
X	RYU KYUNGSUN ET AL: "Chemical etching of boron-rich layer and its impact on high efficiency n-type silicon solar cells", APPLIED PHYSICS LETTERS, AMERICAN INSTITUTE OF PHYSICS, US, deel 101, nr. 7, 13 augustus 2012 (2012-08-13), bladzijden 73902-73902, XP012164755, ISSN: 0003-6951, DOI: 10.1063/1.4746424 [gevonden op 2012-08-14]	1,3, 5-10, 14-20
Y	* het gehele document *	11-13

-/--

[X] Verdere documenten worden vermeld in het vervolg van vak C.

[X] Leden van dezelfde octrooifamilie zijn vermeld in een bijlage

° Speciale categorieën van aangehaalde documenten

"A" niet tot de categorie X of Y behorende literatuur die de stand van de techniek beschrijft

"D" in de octrooiaanvrage vermeld

"E" eerdere octrooi(aanvrage), gepubliceerd op of na de indieningsdatum, waarin dezelfde uitvinding wordt beschreven

"L" om andere redenen vermelde literatuur

"O" niet-schriftelijke stand van de techniek

"P" tussen de voorrangsdatum en de indieningsdatum gepubliceerde literatuur

"T" na de indieningsdatum of de voorrangsdatum gepubliceerde literatuur die niet bezwarend is voor de octrooiaanvrage, maar wordt vermeld ter verheldering van de theorie of het principe dat ten grondslag ligt aan de uitvinding

"X" de conclusie wordt als niet nieuw of niet inventief beschouwd ten opzichte van deze literatuur

"Y" de conclusie wordt als niet inventief beschouwd ten opzichte van de combinatie van deze literatuur met andere geciteerde literatuur van dezelfde categorie, waarbij de combinatie voor de vakman voor de hand liggend wordt geacht

"&" lid van dezelfde octrooifamilie of overeenkomstige octrooipublicatie

Datum waarop het onderzoek naar de stand van de techniek van internationaal type werd voltooid	Verzenddatum van het rapport van het onderzoek naar de stand van de techniek van internationaal type
20 oktober 2014	

Naam en adres van de instantie	De bevoegde ambtenaar
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Persat, Nathalie

Formulier PCT/ISA/201 (tweede blad) (Januari 2004)

ONDERZOEKSRAPPORT BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE

Nummer van het verzoek om een onderzoek naar de stand van de techniek
NL 2012212

C.(Vervolg). VAN BELANG GEACHTE DOCUMENTEN

Categorie °	Geciteerde documenten, eventueel met aanduiding van speciaal van belang zijnde passages	Van belang voor conclusie nr.
X	VETTER M ET AL: "Investigation of the Surface Passivation of P+-Type Si Emitters by PECVD Silicon Carbide Films", CONFERENCE RECORD OF THE 2006 IEEE 4TH WORLD CONFERENCE ON PHOTOVOLTAIC ENERGY CONVERSION (IEEE CAT. NO.06CH37747), IEEE, 1 mei 2006 (2006-05-01), bladzijden 1271-1274, XP031007546, ISBN: 978-1-4244-0016-4 * het gehele document *	1-4,6,7, 14,15,19
Y	ARMIN RICHTER ET AL: "Boron Emitter Passivation With Al2O3 and Al2O3/SiNx Stacks Using ALD Al2O3", IEEE JOURNAL OF PHOTOVOLTAICS, I E E E, US, deel 3, nr. 1, 1 januari 2013 (2013-01-01) , bladzijden 236-245, XP011482201, ISSN: 2156-3381, DOI: 10.1109/JPHOTOV.2012.2226145 * samenvatting *	11-13
A,D	WO 2008/039067 A2 (ECN ENERGIEONDERZOEK CT NEDERL [NL]; KOMATSU YUJI [NL]; GEERLIGS LAMBE) 3 april 2008 (2008-04-03) in de aanvraag genoemd * het gehele document *	1,19,20
A,D	MICHAEL ANDREAS KESSLER ET AL: "Charge carrier lifetime degradation in Cz silicon through the formation of a boron-rich layer during BBr3 diffusion processes; Charge carrier lifetime degradation in Cz silicon through the formation of a BRL during BBr3 diffusion processes", SEMICONDUCTOR SCIENCE AND TECHNOLOGY, IOP PUBLISHING LTD, GB, deel 25, nr. 5, 1 mei 2010 (2010-05-01), bladzijde 55001, XP020172915, ISSN: 0268-1242 in de aanvraag genoemd * het gehele document *	1-20
A,D	MÜLLER RALPH ET AL: "Evaluation of implantation annealing for highly-doped selective boron emitters suitable for screen-printed contacts", SOLAR ENERGY MATERIALS AND SOLAR CELLS, deel 120, 10 juli 2013 (2013-07-10), bladzijden 431-435, XP028775044, ISSN: 0927-0248, DOI: 10.1016/J.SOLMAT.2013.06.040 in de aanvraag genoemd * het gehele document *	1-20

2

ONDERZOEKSRAPPORT BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE

Informatie over leden van dezelfde octrooifamilie

Nummer van het verzoek om een onderzoek naar de stand van de techniek
NL 2012212

In het rapport genoemd octrooigeschrift	Datum van publicatie	Overeenkomend(e) geschrift(en)		Datum van publicatie
WO 2008039067	A2 03-04-2008	AT	492908 T	15-01-2011
		AU	2007300831 A1	03-04-2008
		CN	101548395 A	30-09-2009
		EP	2070128 A2	17-06-2009
		ES	2359531 T3	24-05-2011
		JP	2010504651 A	12-02-2010
		KR	20090088860 A	20-08-2009
		MY	145709 A	30-03-2012
		NL	2000248 C2	26-03-2008
		PT	2070128 E	01-04-2011
		TW	200818535 A	16-04-2008
		US	2010154883 A1	24-06-2010
		WO	2008039067 A2	03-04-2008

WRITTEN OPINION

File No.	Filing date *(day/month/year)*	Priority date *(day/month/year)*	Application No.
SN61937	06.02.2014		NL2012212

International Patent Classification (IPC)
INV. H01L31/0216 H01L31/18

Applicant
Stichting Energieonderzoek Centrum Nederland

This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the application
- ☒ Box No. VIII Certain observations on the application

	Examiner
	Persat, Nathalie

WRITTEN OPINION

Box No. I Basis of this opinion

1. This opinion has been established on the basis of the latest set of claims filed before the start of the search.

2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the application and necessary to the claimed invention, this opinion has been established on the basis of:

   a. type of material:

   ☐ a sequence listing

   ☐ table(s) related to the sequence listing

   b. format of material:

   ☐ on paper

   ☐ in electronic form

   c. time of filing/furnishing:

   ☐ contained in the application as filed.

   ☐ filed together with the application in electronic form.

   ☐ furnished subsequently for the purposes of search.

3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

4. Additional comments:

Box No. V Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty	Yes:	Claims	10-13
	No:	Claims	1-9, 14-20
Inventive step	Yes:	Claims	
	No:	Claims	1-20
Industrial applicability	Yes:	Claims	1-20
	No:	Claims	

2. Citations and explanations

see separate sheet

WRITTEN OPINION

Box No. VIII Certain observations on the application

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1 Reference is made to the following documents:

D1 RYU KYUNGSUN ET AL: "Chemical etching of boron-rich layer and its impact on high efficiency n-type silicon solar cells", APPLIED PHYSICS LETTERS, deel 101, nr. 7, 13 augustus 2012 (2012-08-13), bladzijden 73902-73902, XP012164755, ISSN: 0003-6951

D2 VETTER M ET AL: "Investigation of the Surface Passivation of P+-Type Si Emitters by PECVD Silicon Carbide Films",CONFERENCE RECORD OF THE 2006 IEEE 4TH WORLD CONFERENCE ON PHOTOVOLTAIC ENERGY CONVERSION, IEEE,1 mei 2006 (2006-05-01), bladzijden 1271-1274, XP031007546, ISBN: 978-1-4244-0016-4

D3 ARMIN RICHTER ET AL: "Boron Emitter Passivation With Al2O3 and Al2O3/SiNx Stacks Using ALDAl2O3, IEEE JOURNAL OF PHOTOVOLTAICS,deel 3, nr. 1, 1 januari 2013 (2013-01-01), bladzijden 236-245, XP011482201, ISSN: 2156-3381

2 The present application does not meet the criteria of patentability, because the subject-matter of claim 1 is not new.

2.1 D1 discloses a:

Werkwijze voor het vervaardigen van een kristallijne silicium zonnecel (Fig. 1 (a)), omvattende
verschaffen van een kristallijn siliciumsubstraat (Cz n-type Si wafer, see p. 101, right column),
verschaffen van een met boor gedoteerde oppervlaktelaag (a boron dopant source was deposited on the front surface, followed by a drive-in, see p. 1 right column) in het kristallijn siliciumsubstraat met een piekboordoteringsconcentratie die hoger is dan 8E19 cm^{-3} (for sample of group II, the layer of diffused boron has not undergone chemical etching treatment, see p. 1, right column; its peak boron concentration is therefore the boron peak concentration just after the boron doping step. The boron concentration is above 1E20 cm^{-3}, see p. 3, left column) ; en verwijderen van een oppervlaktedeel van de met boor gedoteerde laag (see p. 1, right column,

a chemical etching treatment is applied for a short period to remove the boron rich layer);
en vormen van een passiveringsfilm op de met boor gedoteerde laag (samples of group IV, having received chemical etching treatment for removing the boron rich layer, are passivated with nitric acid-grown oxide capped with SiNx, see p. 1);
resulterend in een oppervlakteboorconcentratie direct onder de passiveringsfilm die hoger is dan 5E19 cm^{-3} (implict disclosure, because the peak boron concentration before the chemical etching is above 1E20 cm^{-3}, corresponding to a p+ emitter sheet resistance of 45 Ω/sq; after the chemical etching of the boron rich layer, the depletion layer is removed and the p+ emitter sheet resistance is 60 Ω/sq, see page 1, right column; the increase of sheet resistance is not significant, indicating that the overall decrease of the boron concentration is moderated, meaning that it is above 5E19 cm^{-3} at the surface directly underneath the passivation).

The subject-matter of claim 1 is therefore not new.

2.2 D2 discloses a:

Werkwijze voor het vervaardigen van een kristallijne silicium zonnecel (see "Introduction"), omvattende
verschaffen van een kristallijn siliciumsubstraat (p. 1271, right column: n-type Cz Si wafer),
verschaffen van een met boor gedoteerde oppervlaktelaag (p. 1272: p+ emitter formed by diffusion under BBr3 atmosphere followed by oxidation/ drive-in) in het kristallijn siliciumsubstraat met een piekboordoteringsconcentratie die hoger is dan 8E19 cm^{-3} (see peak of boron concentration in Fig. 2) ; en verwijderen van een oppervlaktedeel van de met boor gedoteerde laag (p. 1272, left column: after the oxidation/drive-in step, the boron rich layer is removed by an etching in HF);
en vormen van een passiveringsfilm op de met boor gedoteerde laag (deposition of SiCx film, see Fig. 1);
resulterend in een oppervlakteboorconcentratie direct onder de passiveringsfilm die
hoger is dan 5E19 cm^{-3} (see Fig. 2, boron concentration above 5E19 cm^{-3} when the boron layer is etched back to "100 Ω/sq").

The subject-matter of claim 1 is therefore also not new.

3 The present application does not meet the criteria of patentability, because the subject-matter of claim 19 is not new.

3.1 As indicated above (item 2.1), D1 discloses the method according to claim 1. D1 therefore also discloses an intermediate surface configuration of a crystalline silicon substrate obtained using the method according to claim 1. The subject-matter of claim 19 is therefore not new.

3.2 As indicated above (item 2.2), D2 discloses the method according to claim 1. D2 therefore also discloses an intermediate surface configuration of a crystalline silicon substrate obtained using the method according to claim 1. The subject-matter of claim 19 is therefore also not new.

4 The present application does not meet the criteria of patentability, because the subject-matter of claim 20 is not new.

As indicated above (item 2.1), D1 discloses the method according to claim 1, thereby obtaining a crystalline silicon solar cell. D1 therefore also discloses a crystalline silicon solar cell obtained using the method of claim 1.

5 Dependent claims 2-18 do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of novelty and/or inventive step:

claim 2: D2 (Fig. 2: when the boron layer is etched back to "100 Ω/sq", the etching depth is 100 nm) discloses "het verwijderde oppervlaktedeel van de met boor gedoteerde laag is tussen 5-200 nm dik"

claim 3: D1 (p. 1, right column) discloses that the boron doped layer is obtained by boron ion implantation. In D2 (p. 1272, left column), it is obtained by thermal diffusion.

claim 4: D2 (p. 1272, left column, diffusion followed by oxidation/drive-in) discloses "de stap van verkrijgen van de met boor gedoteerde oppervlaktelaag wordt gevolgd door thermische oxidatie".

claim 5: According to D1 (Fig. 4, p. 2, left column), the boron detection limit of AES is about 1E20 cm^{-3}. In Fig. 4, a boron peak is significant, indicating the presence of a boron rich layer.

claim 6: D1(p. 1, right column) discloses wet chemical etching to remove partly the boron diffused layer. D2 also discloses wet chemical etching (p. 1272, left column).

claim 7: D1(p. 1, right column) discloses a sheet resistance of the boron doped layer after etching of 60 Ω/sq. In D2 (Fig. 2), the sheet resistance value is 100 Ω/sq.

claims 8-10, 17: D1 (p. 1) discloses that the passivation film is a nitric acid-grown oxide (thereby, a silicon oxide film is formed) capped by a SiNx film.

claims 11-13: D3 (abstract), also related to the passivation of a boron doped layer in crystalline silicon, discloses that aluminium oxide formed by ALD has excellent passivation effects on such layers.

claims 14-15: D1 (Fig. 1, p. 1, right column) discloses that the boron doped layer is an emitter layer in a silicon solar cell. Obviously, the method is also suitable for forming a back or front surface field layer.

claim 16: D1 discloses forming a phosphorous doped layer on the back of the solar cell where boron doped layer is not present (p. 1, right column, Fig. 1).

claim 18: D1 (p. 1, right column) discloses surface texturing before forming a boron doped layer.

Re Item VIII

Certain observations on the application

Claims 5, 8, 11, 19 and 20 are not clear.

The relative term "een rijke boorlaag" used in claim 5 has no well-recognized meaning and leaves the reader in doubt as to the meaning of the technical feature to which it refers, thereby rendering the definition of the subject-matter of said claim unclear.

The relative terms "een dunne siliciumoxidefilm" and "dunne siliciumoxide" used in claims 8 and 11 has no well-recognized meaning and leaves the reader in doubt as to the meaning of the technical feature to which it refers, thereby rendering the definition of the subject-matter of said claims unclear.

The features in the product claims 19 and 20 relate to a method of manufacturing the product rather than clearly defining the product in terms of its technical features. The intended limitations are therefore not clear from these claims.