METHOD FOR IMPROVED PASSIVATION AND SOLAR CELL WITH IMPROVED PASSIVATION

This invention relates to a production method of wafer based solar panels, and which the cells obtain an improved field passivation effect and solar cells with improved field passivation effects, where the method comprises placing the silicon semiconductor in the deposition chamber of a dielectric chemical vapor deposition equipment, introducing precursor gases for forming a silicon nitride film on the exposed surface of the silicon semiconductor into the deposition chamber, initiating deposition of a silicon nitride film on the silicon semiconductor, doping the deposited silicon nitride film by introducing at least one gaseous compound containing an element which acts as an acceptor element into the precursor gases in the deposition chamber, and continuing depositing the silicon nitride film until the film obtains a thickness in the range of 2 - 500 nm. The invention also relates to solar cells made by the method.
Method for improved passivation and solar cell with improved passivation

This invention relates to a production method of wafer based solar panels, and which the cells obtain an improved field passivation effect and solar cells with improved field passivation effects.

Background

The world supplies of fossil oil are expected to be gradually exhausted in the following decades. This means that our main energy source for the last century will have to be replaced within a few decades, both to cover the present energy consumption and the coming increase in the global energy demand.

In addition, there are raised many concerns that the use of fossil energy is increasing the earth greenhouse effect to an extent that may turn dangerous. Thus the present consumption of fossil fuels should preferably be replaced by energy sources/carriers that are renewable and sustainable for our climate and environment.

One such energy source is solar light, which irradiates the earth with vastly more energy than the present and any foreseeable increase in human energy consumption. However, solar cell electricity has up to date been too expensive to be competitive with present grid power made by nuclear power, thermal power etc. This needs to change if the vast potential of the solar cell electricity is to be realised.

The cost of electricity from a solar panel is a function of the energy conversion efficiency and the production costs of the solar panel. Obviously, the search for cheaper solar electricity should thus be focused at high-efficient solar cells made by cost-effective manufacturing methods. Presently, the main production of solar cells is based on silicon as the photovoltaic material, and silicon based solar cells are expected to be the mainstay in the foreseeable future.

Prior art

One important factor for enhancing the energy conversion efficiency of solar cells is electric insulation of the surface of the semiconductor. This is known as surface passivation of the solar cell, and is obtained by depositing one or more layers of a dielectric in order to reduce/avoid recombination of charge carriers at the interface between the deposited dielectric surface and semiconductor. This is becoming progressively more important by use of thinner and thinner wafers/-films as the semiconducting layer in solar cells.

A thin layer of silicon dioxide, SiO₂, may provide excellent surface passivation exhibiting very low surface recombination velocities of solar cells. However, the deposition of the SiO₂-layer involves long processing times and use of high
temperatures in the range of 800 - 1200 °C which may give thermal degrading of the bulk Si-material of the solar cell and alteration of the pn-junction due to indiffusion of contamination elements.

The focus of the photovoltaic industry [1, 2] has thus shifted towards use of amorphous films based on hydrogenated silicon compounds such as amorphous silicon, amorphous silicon dioxide, amorphous silicon nitride, and amorphous silicon carbide. These films may be deposited at low temperature (< 500 °C) at high-throughput rates and exhibits in addition to excellent surface passivation a suited refractive index for an anti-reflective coating (ARC) of solar cells.

One of the most studied amorphous films for use in solar cells are amorphous hydrogenated silicon nitride films, Si$_x$N$_{y}$:H$_z$ (hereafter referred to as SiN$_x$-films). These films may be deposited by use of plasma enhanced chemical vapour deposition (PECVD) at temperatures around 400 °C by use of silane gas and other reactant gases such as ammonia or nitrogen.

Lauinger et al. [3, 4], has shown that there is a correlation between the refractive index of the SiN$_x$-films and their ability to passivate the silicon surface. They found that silicon rich SiN$_x$-films with a refractive index greater than 2.3 provide the maximum surface passivation. However, silicon rich SiN$_x$-films exhibit absorption in the UV-range leading to a reduction in the short-circuit current, high resilience towards etching fluids leading to problems with local opening of the film in subsequent process steps, and need for high concentrations of the toxic and self-igniting and explosive silane gas in the PECVD-chamber.

Kerr [1] has shown that using stoichiometric films of amorphous hydrogenated silicon nitride films rather than silicon rich silicone nitride films, solves the problem with UV-range absorption and excessive resilience towards etching agents. Stoichiometric SiN$_x$-films are also shown to have excellent passivation properties.

The low surface recombination velocities of Si/SiN$_x$ interfaces are probably due to two different reasons. The first reason is saturation of dangling bonds at the interface by atomic hydrogen released from the precursor gases (SiH$_4$ and NH$_3$), giving an effect due to decreased interface state density. The second reason is due to fixation of a high density of positive charges in the deposited SiN$_x$-films, giving rise to a field-effect passivation. According to Weber and Jin [5], the fixation of positive charges in PECVD deposited SiN$_x$-films is due to an over-stoichiometric ratio of silicon in the precursor gases during the deposition of the film, typically giving a density of positive charge in the film in the order of $10^{12}$ cm$^{-2}$. The silane is decomposed into positively charged ions (cationic gas) and ammonia is decomposed into negatively charged ions (anionic gas).
However, when SiN$_x$-films with excess of positive fixed charges are applied on p-doped semiconductors, the field effect of the positive charges will serve to attract negative charges to the surface boundary region of the semiconductor and thus create a negatively charged layer underneath the SiN$_x$-film. This layer is known as an inversion layer. The inversion layer in p-doped semiconductors is known to create problems at the metal contacts on the back/rear of the cells, due to a short circuit effect in the vicinity of the electrode which reduces the collected current of the rear side of the solar cell. This short circuiting effect is known as parasitic shunting.

Dauwe et al. [6] performed experiments on 1.5 $\Omega$cm FZ p-type silicon cells illuminated by AM1.5G 100 mW/cm$^2$ at 25 °C. The tests were made for cells provided with a SiO$_2$ rear side passivation film and compared the cells energy conversion efficiency with similar cells provided with a PECVD deposited SiN$_x$ rear side passivation film. They found that the parasitic shunting effect reduced the cell energy conversion efficiency from 17.9 percent points with SiO$_2$-passivation film to 16.8 percent points with SiN$_x$ passivation film, a loss of 6.2 %. They showed further that by inserting a silicon oxide zone in the SiN$_x$ rear side passivation layer acting to electrically insulating the rear side electric contacts from the inversion layer, the parasitic shunting effect was almost eliminated giving a cell efficiency of 17.8 percent points.

Hoex et al. [7] shows from lifetime measurements, including a direct experimental comparison with thermal SiO$_2$, a-Si:H, and as-deposited a-SiN$_x$-H, that Al$_2$O$_3$, which contains negative charges, provides an excellent level of surface passivation on highly B-doped c-Si with doping concentrations around 10$^{19}$ cm$^{-3}$. The Al$_2$O$_3$ films, synthesized by plasma-assisted atomic layer deposition and with a high fixed negative charge density, limit the emitter saturation current density of B-diffused p+-emitters to $\sim$10 and $\sim$30 fA/cm$^2$ on $>100$ and 54 $\Omega$/sq sheet resistance p+-emitters, respectively. These results demonstrate that highly doped p-type Si surfaces can be passivated effectively with negatively charged films.

WO 02/41408 discloses a method for removing the inversion layer in rear surface SiO$_2$ passivated cells by depositing a fluoride layer with negative charges onto the SiO$_2$-film.

Weber and Jin [5] teaches a method where a corona discharge is used to create and store negative charge in the silicon nitride films of silicon dioxide/silicon nitride stacks. Effective lifetime measurements on both textured and planar, as well as both boron diffused and non-diffused silicon samples passivated with silicon oxide/silicon nitride stacks, show that the creation of negative charge in the nitride layer results in an improvement in the surface passivation for all
samples, with very low (<2 cm/s) effective surface recombination velocities demonstrated for planar, non-diffused samples. The manipulation of charge can be exploited to improve the conversion efficiency of silicon solar cells.

Thus, from a cost- and process perspective, it would be advantageous to surface passivate and form the anti-reflective coating on solar cells by employing an amorphous near-stoichiometric silicon nitride film deposited by plasma enhanced chemical vapour deposition and which has introduced sufficient negative charges to remove the inversion layer.

US 2007/0082507 discloses a method for and apparatus for depositing boron doped silicon nitride films, by introducing a mixture of silane, ammonium and boron-containing gas in the deposition chamber. Other prior art showing that it is possible to boron dope silicon nitride is i.e. US 2006/0032443 and EP 0 394 054. None of these documents are specific on the crystallinity, nitrogen content or doping level of the films. Also, these patents do not describe any electronic properties of the film, they focus only on the mechanical properties of the doped film.

Hasegawa et al. [8] has demonstrated that it is possible to introduce doping element boron into microcrystalline SiN$_x$:H-films and thus change the electrical properties of the film. However, for amorphous SiN$_x$:H-films and amorphous SiC$_x$:H-films, Hasegawa informs the boron doping efficiency is reduced with increasing doping level, increasing nitrogen level, and decreasing crystallinity in the SiN$_x$:H-films.

The findings of Hasegawa [8] is consistent with the theory of doping of crystalline silicon which is based on the idea that silicon can covalently bond four neighbouring atoms, while the dopants can only bond three. In an amorphous silicon structure this explanation does not hold, as there exists atoms bonded to both three and four neighbours. If we assume that the dopant atoms will prefer the 3-bonded sites, which they probably would in a perfect equilibrium, doping should be impossible. Hasegawa's work also seems to exclude amorphous stoichiometric nitride as a good candidate for boron doping. Still experiments show that amorphous silicon can be doped, but with a much lower doping efficiency than crystalline silicon. However, because an amorphous silicon nitride will have a much higher number of 3-bonded atoms, and because these will often be nitrogen, not silicon, there is every reason to assume that the doping efficiency will be much lower in amorphous silicon nitride than in amorphous silicon, and no convincing reason to assume that significant electrical doping is actually possible.

Also, the extensive use of amorphous silicon nitride as a passivation layer is to a large extent related to the positive charge found in a silicon-SiN interface. This charge is assumed to be due to the K-point defect - a defect consisting of to neighbouring dangling bonds both passivated by hydrogen. Such a defect can be in one of three
states, with two electrons (negatively charged), with one electron (neutral) or with no electrons (positive charge). This defect type has been proposed as the source of the strong hysteresis behaviour seen in CV-measurements of amorphous silicon nitrides; see i.e. Beylier et al. [9]. The reported hysteresis behaviour may be explained by the fact that the K-point defect can change its charge based on the charge of the surroundings.

Thus in order to employ the cost effective solution of introducing n-dopants into a combined passivation layer and anti-reflective cover of silicon nitride formed by chemical vapour deposition, it will be necessary to obtain a sufficiently heavy doping to overcome the inherent positive charges of CVD-formed SiN_x-films and the expected charge compensation resulting from the strong hysteresis behaviour of these films. However, from Hasegawa et al. [8], it is difficult to obtain such heavy n-doping of amorphous nitrogen rich SiN_x-films.

Objective of the invention
The main objective of the invention is to provide a cost effective industrially applicable method for passivation of p-type doped silicon based solar cells.

The objective of the invention may be realised by the features as set forth in the description of the invention below, and/or in the appended patent claims.

Description of the invention
The invention is based on the realisation that a cost effective industrial applicable method of forming a passivation film with similar excellent passivation properties as the passivation films with negative charge in the prior art above, may be obtained if the negative charge in the passivation layer may be introduced during presently industrially employed deposition processes based on chemical vapour deposition. That is, the invention is the exploitation of the discovery that in contradiction to the reaching of Hasegawa and expectations from doping theory, that introduction of precursor gases containing n-type dopant elements together with the passivation film forming precursor gases in a chemical vapour deposition chamber, may form an amorphous silicon nitride film with sufficient n-type doping to remove the inversion layer in p-type doped silicon.

Thus in a first aspect, the present invention relates to a method for surface passivation of a silicon semiconductor, where the method comprises:
- placing the silicon semiconductor in the deposition chamber of a chemical vapour deposition equipment,
- introduce precursor gases for forming a silicon nitride film on the exposed surface of the silicon semiconductor into the deposition chamber,
- initiate deposition of a silicon nitride film on the silicon semiconductor,
- doping the deposited silicon nitride film by introducing at least one gaseous compound containing an element which acts as an acceptor element into the precursor gases in the deposition chamber, and
- continue depositing the silicon nitride film until the film obtains a thickness in the range of 2 - 500 nm.

The doped silicon nitride layer of the first aspect of the invention functions as a combined field effect passivation layer and chemical passivation layer. As an alternative, it may be applied a first dielectric layer functioning as a chemical passivation layer, followed by a second dielectric layer providing the field effect passivation of the semiconductor surface. That is, the first dielectric layer is not doped, while the second dielectric layer is doped to obtain the field passivation effect.

Thus in this alternative embodiment, the first passivation layer may be any known or conceivable dielectric layer with a chemical passivation effect on silicon semiconductor surfaces, such as i.e. silicon dioxide, SiO₂; hydrogenated amorphous silicon, a-Si:H, hydrogenated amorphous silicon nitride, a-SiNx:H; hydrogenated amorphous silicon carbide, a-SiCx:H etc. The second dielectric layer may be a n-type doped dielectric layer of amorphous silicon nitride, a-SiNx, or hydrogenated amorphous silicon nitride, a-SiNx:H. The a-SiNx or a-SiNx:H may advantageously be nitrogen rich, that is the nitrogen content of the film may advantageously be near stoichiometric or more. The term "near stoichiometric or more" as used herein, means that the "x" in SiNx or SiNx:H has a value of x = 1 or larger, preferably x = 1.2 or larger, and more preferably x = 1.3 or larger. Stoichiometric silicon nitride has chemical formula Si₃N₄, and corresponds to x = 1.33. That is, the term "x" as used herein means the atomic ratio N/Si in the dielectric layer.

It may also be applied a third dielectric layer. This third layer may, as the first dielectric layer, be of any known or conceivable dielectric layer with a chemical passivation effect on silicon semiconductor surfaces, such as i.e. silicon dioxide, SiO₂; hydrogenated amorphous silicon, a-Si:H, hydrogenated amorphous silicon nitride, a-SiNx:H; hydrogenated amorphous silicon carbide, a-SiCx:H etc. The nitrogen content of the film may advantageously be near stoichiometric or more.

In another embodiment, it is envisioned employing a first and third layer of SiNx or SiNx:H, an a second layer of n-type doped hydrogenated amorphous silicon, a-Si:H.

Thus the first aspect of the invention obtains introduction of negative charges in the passivation film (silicon nitride or silicon film) by introducing atoms which functions as electron acceptors in the film. Negative charges in the silicon nitride or silicon film will attract positive charges to the wafer surface; in just the same
manner as positive charges in the passivation film attracts negative charges and
creates an inversion layer. The negative charges of the passivation film at the p-
type doped surface of the wafer will reduce minority carrier recombination by
providing an increased field passivation effect. The layer of positive charges in
the surface region of the semiconductor wafer may be considered as an opposite
of an inversion layer, known as, an accumulation layer, and will be denoted "the
positive charged layer" in this application.

In a second aspect, the invention relates to solar cells, where the solar cells
comprises:
- a silicon semiconductor wafer or film where at least the rear surface,
alternatively both front and rear surfaces, have at least one layer of silicon nitride
deposited by chemical vapour deposition,
- the silicon nitride film contains an element which acts as an acceptor element in
the film and thus form negatively charged film, and where
- the concentration of dopants in the silicon nitride film results in a negative
charge of the film in the range from $10^9$ to $10^{15}$ cm$^{-2}$.

The concentration of dopants in the amorphous silicon nitride film, or
alternatively in the amorphous silicon film, may advantageously be in the range
from $10^{10}$ to $10^{15}$ cm$^{-2}$, or more advantageously from $10^{12}$ to $10^{15}$ cm$^{-2}$.

As an alternative of the second aspect of the invention, the solar cell my have a
first dielectric layer functioning as a chemical passivation layer, followed by a
second dielectric layer providing the field effect passivation of the
semiconductor surface. That is, the first dielectric layer is not doped, while the
second dielectric layer is doped to obtain the field passivation effect. This may
be obtained by employing any known or conceivable dielectric layer with a
chemical passivation effect on silicon semiconductor surfaces, such as i.e. silicon
dioxide, SiO$_2$; hydrogenated amorphous silicon, a-Si:H, hydrogenated
amorphous silicon nitride, a-SiN$_x$:H; hydrogenated amorphous silicon carbide, a-
SiC$_x$:H etc. as the first passivation layer. The second dielectric layer of the solar
cell may then be a n-type doped dielectric layer of amorphous silicon nitride, a-
SiN$_x$, or hydrogenated amorphous silicon nitride, a-SiN$_x$:H. The a-SiN$_x$ or a-
SiN$_x$:H may advantageously be nitrogen rich, that is the nitrogen content of the
film may advantageously be near stoichiometric or more. The solar cell may also
have a third dielectric layer. This third layer may, as the first dielectric layer, be
of any known or conceivable dielectric layer with a chemical passivation effect
on silicon semiconductor surfaces, such as i.e. silicon dioxide, SiO$_2$;
hydrogenated amorphous silicon, a-Si:H, hydrogenated amorphous silicon
nitride, a-SiN$_x$:H; hydrogenated amorphous silicon carbide, a-SiC$_x$:H etc. The
nitrogen content of the film may advantageously be near stoichiometric or more.
As a further alternative, the solar cell may have a first and third layer of SiN$_x$ or
SiN$_x$:H, an a second layer of n-type doped hydrogenated amorphous silicon, a-Si:H.

The invention will practically eliminate the parasitic shunting effect and obtain the beneficial combined effect of the excellent chemical passivation effect of the silicon nitride film and the field passivation effect of the fixed positive layer. Another advantage is that this effect may be obtained by employing presently implemented infrastructure for deposition of passivation films in the photovoltaic industry, and thus constituting a very cost effective solution to the problem of parasitic shunting which may relatively easily be implemented in existing production lines.

The term "acceptor" as used herein means any dopant atom added to the silicon nitride film which can contribute to form a negatively charged film. The formation of negatively charged regions in the film is believed to be due to substitution of a silicon atom in the silicon nitride film with a dopant atom which has at least one less valence electron than the silicon atom. This substitution will result in formation of one or more molecular orbitals in one neighbouring silicon atom in the film with an electron vacancy, and this unsatisfied bond will extract an electron from the surroundings and thus form a silicon atom in the film with a net negative charge and thus form the negatively charged regions of the film. Boron and aluminium are examples of suitable dopants.

The silicon nitride film may be doped by simply mixing the silicon nitride forming precursor gases with the dopant forming gas (for instance a boron or aluminium containing gas) in the deposition chamber during the entire deposition of the silicon nitride film. In embodiments where the surface passivation is obtained by depositing more than one dielectric layer, it is envisioned forming only a doped layer into the silicon nitride film, or alternatively into the amorphous silicon film. This may be obtained by introducing the dopant gases into the deposition chamber for only a period of the deposition process. The thickness of the doped layer and the dopant density in the layer may be controlled by regulating the time period when the dopant gases are introduced into the deposition chamber and the concentration of the dopant gases in the deposition chamber of the deposition equipment, respectively.

The invention may apply any known or conceivable chemical vapour deposition technique known to be able to form a silicon nitride film. Suitable deposition techniques includes, but are not limited by, Atmospheric pressure CVD (APCVD), Low-pressure CVD (LPCVD), Ultrahigh vacuum CVD (UHVCVD), Aerosol assisted CVD (AACVD), Microwave plasma-assisted CVD (MPCVD), Plasma-Enhanced CVD (PECVD), Remote plasma-enhanced CVD (RPECVD),
Atomic layer CVD (ALCVD), Hot wire CVD (HWCVD), Catalytic CVD (Cat-CVD), hot filament CVD (HFCVD).

The invention may apply any known or conceivable precursor gas able to form silicon nitride by chemical vapour deposition. Examples of suitable precursor gases includes, but are not limited by, SiH₄, SiCl₂H₂, N₂, and NH₃. The chemical reactions involved may be given as:

\[
\begin{align*}
3\text{SiH}_4 + 4\text{NH}_3 & \rightarrow \text{Si}_3\text{N}_4 + 12\text{H}_2 \\
3\text{SiCl}_2\text{H}_2 + 4\text{NH}_3 & \rightarrow \text{Si}_3\text{N}_4 + 6\text{HCl} + 6\text{H}_2 \\
2\text{SiH}_4 + \text{N}_2 & \rightarrow 2\text{SiNH} + 3\text{H}_2 \\
\text{SiH}_4 + \text{NH}_3 & \rightarrow \text{SiNH} + 3\text{H}_2
\end{align*}
\]

The dopant forming gases may be any chemical compound which is in the gas phase at the conditions experienced in the deposition chamber of chemical vapour deposition equipment, and which acts as an acceptor in the amorphous silicon nitride or amorphous silicon layer. Examples of suited compounds include any gaseous compound containing an element from group III of the periodic table. The compound should preferably be a nitride or a hydride of the group III element in order to avoid introducing "foreign" or in any way polluting elements into the deposition chamber. Diborane, B₂H₆, is an example of such a compound, and which is suitable for forming the p-type doped silicon nitride film according to the first aspect of the invention.

The inventive idea of employing a dopant forming gas in the deposition chamber which provides a negatively charged silicon nitride film may also be applied to other films than silicon nitride. In this case the precursor gases forming the film are admixed with a dopant gas in the same manner as the precursor gases forming the silicon nitride film. The use of other negatively doped films may also be combined with the silicon nitride film according to the first or second aspect of the invention.

One example of a high efficient and much employed dielectric film on silicon based solar cells is silicon dioxide, SiO₂. Silicon dioxide may be applied by chemical vapour deposition using silane and nitrous oxide, N₂O, at temperature in the deposition chamber between 50 - 500 °C. It is also possible to employ dichlorosilane, SiCl₂H₂, oxygen, O₂, or an organic silicon compound. Possible chemical reactions are:

\[
\begin{align*}
\text{SiH}_4 + \text{N}_2\text{O} & \rightarrow \text{SiO}_2 + 2\text{H}_2 + 2 \text{N}_2 \\
\text{SiCl}_2\text{H}_2 + 2\text{N}_2\text{O} & \rightarrow \text{SiO}_2 + 2\text{N}_2 + 2\text{HCl}
\end{align*}
\]

By mixing a gas containing an element which acts as acceptor in the silicon dioxide film into the precursor gases, it is obtained a negatively charged silicon
dioxide dielectric film which will form an accumulator layer in the surface region of the silicon semiconductor. The dopant forming gas may i.e. be B$_2$H$_6$. Typical thickness of the doped silicon oxide film will be from 10 to 200 nm, but may also be outside this range.

The invention may apply any conceivable dielectric film suited to be used as surface passivation on silicon semiconductors and which may be deposited by chemical vapour deposition.

It is envisioned that the silicon dioxide passivation film may be applied as the only passivation film or in combination with the silicon nitride layer of the first and second aspect of the invention.

Another example of suited passivation layer is hydrogenated amorphous silicon, a-Si:H, which may be formed by chemical vapour deposition of silane gas at a temperature in the deposition chamber of 50-500 °C:

$$\text{SiH}_4 \rightarrow \text{a-Si:H} + 2\text{H}_2$$

The film may be doped by introduction of a boron containing gas, i.e. diborane, B$_2$H$_6$. It is envisioned that the hydrogenated silicon film may be used in combination with silicon dioxide, silicon nitride or both. Typical thickness of the doped hydrogenated amorphous silicon film will be from 2 to 200 nm, but may also be outside this range.

**List of figures**

Figure 1 is a schematic drawing of an example embodiment of the present invention seen from the side.

Figure 2a shows the measured C-V curves from -6V to 0V for test samples BO-B7.

Figure 2b shows the measured C-V curves from -6V to +6V for test samples BO—B7.

Figure 3a shows the measured FTIR-curves for test samples BO—B7.

Figure 3b is an enlargement of a part of the curves shown in figure 3a.

**Example embodiment**

An example embodiment of a solar cell made according to the invention is presented in Figure 1.

The Figure shows a silicon semiconductor wafer 1 which is doped to form a front side layer 2 of n-type doping and a rear side layer 3 of p-type doping. The front side is provided with one dielectric layer 4 of silicon nitride and a grid of front side electric contacts 5 establishing electric contact with the n-type doped layer 2.
The rear side is provided with a first dielectric layer 6 of silicon dioxide and a second dielectric layer 7 of silicon nitride. The back side is provided with a metallic layer 8 forming the back side electric contact. The electric contact 8 is made with protrusions 9 which locally extend through the dielectric layers in order to make contact with the p-type doped layer 3.

An inversion layer 10 is also indicated in the Figure. In case of prior art which employs a non-doped silicon nitride dielectric layer 7, the inversion layer will be negatively charged and will thus result in parasitic shunting due to contact with the positive contact 9. However, by employing a doped silicon nitride layer 7 according to this invention, the inversion layer 10 will be inverted to form an accumulation layer which increases the current density of the solar cell. The contact between an accumulation layer 10 and electric contact 9 is no longer a problem, it is an asset.

The silicon nitride dielectric layer 7 is deposited by use of plasma enhanced chemical vapour deposition by use of SiH₄ and NH₃ as precursor gases admixed with B₂H₆. The deposition process is run at a temperature in the deposition chamber in the range from 250 to 450°C, and the process is run until a thickness of the silicon nitride dielectric layer 7 is in the range between 40-200 nm is obtained.

Verification of the invention

In order to verify the invention, a series of capacitance-voltage measurements have been made on a passivation layer according to the first aspect of the invention laid down on wafers of p-type doped, 1 - 30 Ohm, mono-crystalline Cz-polished silicon.

The procedure for forming the passivation layers was: The wafers were first cleaned by immersion for 2 minutes in a 5% aqueous solution of fluoric acid. Then the wafers were transferred to an Oxford type plasma enhanced vapour deposition chamber. The PECVD was performed at a temperature of 400°C. The silicon nitride film was made by feeding the deposition chamber with a flow of 50 sccm of NH₃ and 17.4 sccm of SiH₄.

The amount of boron introduced into the film was varied by varying the feed rates of the boron-containing gas, which was diborane, B₂H₆, diluted in helium gas to a diborane-concentration of 2 weight%. The PECVD-deposition was maintained for four minutes in each sample. For each test, the pressure in the deposition chamber was adjusted to maintain the same partial pressures of NH₃ and SiH₄. The feed rates of diborane and pressures employed are given in Table 1. The thickness of each of the deposited boron-doped layers was measured by ellipsometry, the values are inserted in Table 1.

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After deposition the wafers went through a normal industrial firing sequence, with a maximum temperature higher than 900 °C in order to create conditions met in industrial production of solar cells with amorphous hydrogenated silicon nitride as surface passivation and anti-reflective coating.

After firing, each sample of the wafers were subject to capacitance-voltage (C-V) measurements by contacting the wafer with deposited nitride film, which may be considered as a stack of c-Si and a-SiN\textsubscript{x}:H, by metallic phases (electric contacts) and applying a low amplitude 100 kHz alternating current signal and imposing a direct current signal sweeping from 0V to -6V, then from -6V to 6V, and then back to -6V. The resulting C-V curves are shown in Figure 2a and 2b. Each sample from B0 to B7 is marked with an "F", i.e. BOF in these figures to indicate that the measurements are performed after firing. The figures show that there is a weak hysteresis for very high positive voltages for the highest doped samples B6 and B7, showing that we can slightly change the charge of the interface. It is therefore assumed that the flat lines shown in the 0V to -6V sweep for sample B6 and B7 (Figure 2a) are because the sample is fully in accumulation for this voltage range, exactly as anticipated for a sample with a large negative charge.

Further, is can clearly be seen on Figures 2a and 2b that the flatband voltage can be no smaller than 4 V for sample B6 and B7. Thus, since the area of the contact is a 1mm diameter dot, the maximum capacitance per area is of the order 2·10^{-8}, giving an estimated charge density greater than 5·10^{-7} C/cm\textsuperscript{2}, or a charge carrier density of greater than 1·10^{-12} m\textsuperscript{2}. This verifies that sample B6 and B7 which are near stoichiometric amorphous silicon nitride films have net negative charge at the p-Si/SiN interface with a charge density of more than 1·10^{-12} m\textsuperscript{2}. These doped nitride films are not structurally very different from the un-doped nitride at the doping levels we have observed, such that the optical characteristics of the doped films are suitable for solar cells, and these results are obtained after firing.

It is also seen on Figures 2a and 2b that for samples B0 (no doping) and B1 (smallest applied doping level), that the zero V point is in the inversion regime. This shows that these silicone nitride films have a positive net interface charge. For samples B2 to B5, which were heavier doped, the zero V point occurred nearer the maximum depletion part of the curves, which is consistent with a smaller net positive charge of the silicon nitride films as compared with the lesser doped films. For sample B6 and B7, which are the heaviest doped samples, the zero V point occurs in the accumulation regime of the curves, which shows that these silicon nitride films have a net negative charge. These results show that a quite heavy doping is needed to overcome the positive charge present in intrinsic a-SiN\textsubscript{x}-films.

These results are supported by Fourier transform infrared spectroscopy (FTIR) measurements of the deposited films in sample B0 to B8. The measurements are
shown in Figure 3a and 3b. There is a clear peak at about 1130 cm⁻¹ in all samples B0 - B7. This peak is due to an Si-O bond. For sample B5, B6, and B7, which are the most heavily doped, also exhibit two peaks at approx. 1180 cm⁻¹ and 1330 cm⁻¹. These peaks are believed to be due to boron incorporation in the film, and it can be seen that the peaks becomes higher with heavier doping.

Table 1  Diborane flow and deposition chamber pressures in verification tests

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Flow B₂H₆/He [scm³/s]</th>
<th>Pressure [mTorr]</th>
<th>Thickness of doped layer [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>B0</td>
<td>0</td>
<td>595</td>
<td>82</td>
</tr>
<tr>
<td>B1</td>
<td>1.5 ± 0.2</td>
<td>604</td>
<td>82</td>
</tr>
<tr>
<td>B2</td>
<td>1.9 ± 0.1</td>
<td>613</td>
<td>82</td>
</tr>
<tr>
<td>B3</td>
<td>3.9 ± 0.1</td>
<td>631</td>
<td>82</td>
</tr>
<tr>
<td>B4</td>
<td>8.0 ± 0.1</td>
<td>666</td>
<td>82</td>
</tr>
<tr>
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References


CLAIMS

1. Method for surface passivation of a silicon semiconductor, where the method comprises:
   - placing the silicon semiconductor in the deposition chamber of a chemical vapour deposition equipment,
   - introduce precursor gases for forming a silicon nitride film on the exposed surface of the silicon semiconductor into the deposition chamber,
   - initiate deposition of a silicon nitride film on the silicon semiconductor,
   - doping the deposited silicon nitride film by introducing at least one gaseous compound containing an element which acts as an acceptor element into the precursor gases in the deposition chamber, and
   - continue depositing the silicon nitride film until the film obtains a thickness in the range of 2 - 500 nm.

2. Method according to claim 1, where
   - the dielectric layer is deposited by use of plasma-enhanced chemical vapour deposition.

3. Method according to claim 2, where
   - the precursor gases are SiH\textsubscript{4} and NH\textsubscript{3},
   - the temperature in the deposition chamber is kept between 50 - 500 °C, and
   - the dopant forming gas is a gaseous compound containing boron.

4. Method according to claim 3 where
   - the precursor gases are SiH\textsubscript{4} and one of N\textsubscript{2}O or an organic silicon containing precursor and O\textsubscript{2},
   - the temperature in the deposition chamber is kept between 50 - 500 °C, and
   - the dopant forming gas is a gaseous compound containing boron.

5. Method according to claim 3 or 4, where dopant forming gas is B\textsubscript{2}H\textsubscript{6}.

6. Method according to claim 5, where
   - the temperature in the deposition chamber is kept between 250 - 400 °C, and
   - the thickness of the deposited film is in the range of 40 - 200 nm.

7. Method according to any of the preceding claims, where the also comprises
   - forming a first dielectric layer onto the semiconductor of amorphous silicon,
amorphous silicon nitride, or silicon dioxide, and then
- depositing a n-type doped silicon nitride layer as the second dielectric layer.

8. Method according to claim 7, wherein the method also comprises forming a third layer of un-doped amorphous silicon nitride as the third passivation layer.

9. Method according to claim 7,
where the deposition of the dielectric layer is performed by
- employing SiH₄ and one of N₂O or an silicon containing organic precursor and O₂ as precursor gases to form a first dielectric layer of SiO₂ on the semiconductor, then
- employing SiH₄, NH₃, and B₂O₆ as precursor gases to form a p-type doped silicon nitride layer onto the first dielectric layer, and then
- employing SiH₄ and NH₃ as precursor gases to form a non-doped silicon nitride layer onto the p-typed doped silicon nitride layer.

10. Solar cell, comprising:
- a silicon semiconductor wafer or film where at least the rear surface, alternatively both front and rear surfaces, have at least one layer of silicon nitride deposited by chemical vapour deposition,
- the silicon nitride film contains an element which acts as an acceptor element in the film and thus form negatively charged film, and where
- the concentration of dopants in the silicon nitride film results in a negative charge of the film in the range from 10⁹ to 10¹⁵ cm⁻².

11. Solar cell according to claim 10, where
- the at least one deposited dielectric film is a silicon nitride film of thickness 2 - 500 nm, and
- which contains elemental boron in a concentration providing a negative charge density in the range from 10⁹ and 10¹⁵ cm⁻².

12. Solar cell according to claim 10, where the semiconductor wafer contains
- a first dielectric layer of amorphous silicon, amorphous silicon nitrode, or silicon dioxide with thickness of 2 - 500 nm,
- a doped silicon nitride layer onto the first dielectric layer, which have thickness in the range of 10 - 200 nm and which is doped with boron in a concentration providing a negative charge density in the range from 10⁹ and 10¹⁵ cm⁻², and
- a final non-doped silicon nitride layer onto the doped silicon nitride layer, and which has thickness in the range from 2 - 500 nm.

13. Solar cell according to claim 10, where the semiconductor wafer contains
- a first dielectric layer of doped amorphous silicon or doped silicon dioxide with thickness of 2 - 500 nm, and which is doped with boron in a concentration providing a negative charge density in the range from 10⁹ and 10¹⁵ cm⁻²,
- a doped silicon nitride layer onto the first dielectric layer, which have thickness in
the range of 10 - 200 nm and which is doped with boron in a concentration providing a negative charge density in the range from $10^9$ and $10^{15}$ cm$^{-2}$, and - a final non-doped silicon nitride layer onto the doped silicon nitride layer, which has thickness in the range from 2 - 500 nm.

14. Solar cell according to claim 10, where the semiconductor wafer contains - a first dielectric layer of doped amorphous silicon or doped silicon dioxide with thickness of 2 - 500 nm, and which is doped with boron in a concentration providing a negative charge density in the range from $10^9$ and $10^{15}$ cm$^{-2}$, and - a doped silicon nitride layer onto the first dielectric layer, which have thickness in the range of 10 - 200 nm and which is doped with boron in a concentration providing a negative charge density in the range from $10^9$ and $10^{15}$ cm$^{-2}$.

15. Solar cell according to claim 10, where the semiconductor wafer contains - a first dielectric layer of doped amorphous silicon or doped silicon dioxide with thickness of 2 - 500 nm, and which is doped with boron in a concentration providing a negative charge density in the range from $10^9$ and $10^{15}$ cm$^{-2}$, and - a non-doped silicon nitride layer onto the doped silicon nitride layer, and which has thickness in the range from 2 - 500 nm.

16. Solar cell according to claim 10, where the semiconductor wafer contains - a first dielectric layer of amorphous silicon with thickness of 2 - 200 nm, - a second dielectric layer of silicon dioxide with thickness of 10 - 200 nm, and - a third dielectric layer of silicon nitride with thickness of 2 - 500 nm, and where - at least one of the first, second or third dielectric layer is doped with boron in a concentration providing a negative charge density in the range from $10^9$ and $10^{15}$ cm$^{-2}$.

17. Solar cell according to any of claims 10 - 16, wherein the doped amorphous silicon nitride layer has a boron concentration providing a negative charge density in the range from $10^{10}$ to $10^{15}$ cm$^{-2}$, or from $10^{12}$ to $10^{15}$ cm$^{-2}$.

18. Use of a doped amorphous silicon nitride layer made by the method of claim 1 to 9 as surface passivation in silicon based solar cells.
**INTERNATIONAL SEARCH REPORT**

**International application No**
PCT/NO2010/000235

**A. CLASSIFICATION OF SUBJECT MATTER**

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According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C23C
HOI

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database consulted during the international search (name of database and, where practical, search terms used)

EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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X Further documents are listed in the continuation of Box C X See patent family annex

- Special categories of cited documents
  - A: document defining the general state of the art which is not considered to be of particular relevance
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  - L: document which may throw doubts on priority claims(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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Date of the actual completion of the international search
10 September 2010

Date of mailing of the international search report
22/09/2010

Name and mailing address of the ISA/Authorized officer
European Patent Office, P B 5818 Patentlaan 2 NL- 2280 HV Rijswijk
Tel (+31-70) 340-2040, Fax (+31-70) 340-3016

Teppo, Kirsi-Marja
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