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(71) **Applicant** *(for all designated States except US)*: **BENEQ OY** [FI/FI]; Ensimmäinen savu, FI-01510 Vantaa (FI).

(72) **Inventors; and**
(75) **Inventors/Applicants** *(for US only)*: **PAKKALA, Arto** [FI/FI]; c/o Beneq Oy, Ensimmäinen savu, FI-01510 Vantaa (FI). **AHONEN, Sampo** [FI/FI]; c/o Beneq Oy, Ensimmäinen savu, FI-01510 Vantaa (FI). **SNECK, Sami** [FI/FI]; c/o Beneq Oy, Ensimmäinen savu, FI-01510 Vantaa (FI). **SKARP, Jarmo** [FI/FI]; c/o Beneq Oy, Ensimmäinen savu, FI-01510 Vantaa (FI). **LI, Shuo** [CN/FI]; c/o Beneq Oy, Ensimmäinen savu, FI-01510 Vantaa (FI).

(74) **Agent**: **PAPULA OY**; Mechelininkatu 1 a, FI-00180 Helsinki (FI).

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(54) Title: A METHOD AND A STRUCTURE FOR PROTECTING A PASSIVATING LAYER

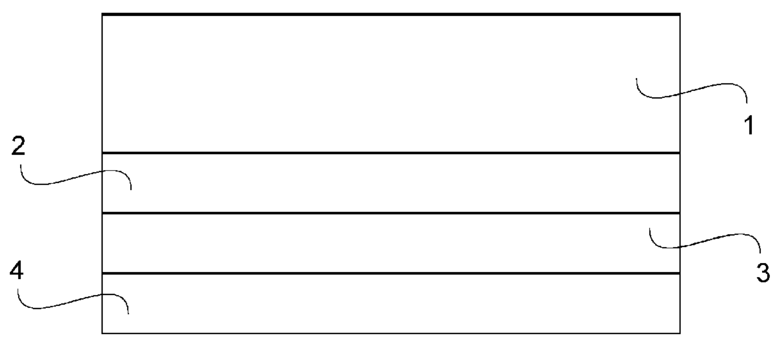

Fig. 2

(57) Abstract: The present invention relates to a method for protecting a passivating layer (2) comprising aluminum oxide and being formed on a surface of a silicon substrate (1) from effects caused by chemical interaction between the passivating layer (2) and a conducting electrode (4) by fabricating a barrier layer (3) between the passivating layer (2) and the conducting electrode (4). Further, the present invention relates to a corresponding structure and its use.

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A METHOD AND A STRUCTURE FOR PROTECTING A PASSIVATING LAYER

FIELD OF THE INVENTION

The present invention relates to a method for protecting a passivating layer and to a structure comprising a barrier layer configured to protect the passivating layer and to the use thereof.

BACKGROUND OF THE INVENTION

Photovoltaic cells are gradually becoming an important means of generating electrical energy. Especially solar cells, photovoltaic cells designed to convert sunlight into electrical energy, are considered as one of the most promising candidates for renewable energy production.

An important issue slowing down the utilization and mitigating the commercial potential of solar cells is their low efficiency relative to their cost, *i.e.* the cost per one watt of installed solar power is high. To reduce the fabrication cost and to improve the efficiency of solar cells, new technologies and new solar cell structures have been developed. One of the improvements in crystalline silicon (c-Si) solar cells has been the introduction of rear surface passivation to reduce the charge carrier recombination on the back side of silicon wafer.

Surface recombination in semiconductors is a result of possibly many different mechanisms leading to trapping of charge carriers in specific energy states at or close to the surface of a semiconductor. These energy states, or surface states as they are often called, may originate from different sources, such as impurities at the surface or the inevitable disruption of periodicity of a semiconductor crystal at the surface. In a photovoltaic cell the quantum efficiency, and therefore the overall efficiency, decreases as charge carriers generated by the absorption of photons in the semiconductor recombine with the surface states and therefore cannot be collected in the cell electrodes to contribute to the cell current.

To reduce surface recombination of charge carriers, several ways of passivating a surface of a semiconductor (or conducting doped semiconductor) have been developed. A promising material candidate for passivating a silicon surface is aluminum oxide. Especially ALD-grown (Atomic Layer Deposition) aluminum oxide has shown to present good passivation on rear surface of p-type silicon solar cells. In the manufacturing of solar cells the back electrode on the aluminum oxide passivating layer can be made of screen printed aluminum, *i.e.* aluminum paste. However, a problem is the relatively weak chemical resistance of amorphous aluminum oxide in the circumstances used in this kind of manufacturing process. This manufacturing method of the back electrode contains a firing step, which is done at an elevated temperature of about 700 – 800 °C. The aluminum paste contains chemicals which etch the passivating layer comprising aluminum oxide and thus causes at least partial removal of aluminum oxide, whereby the surface passivation is weakened or destroyed.

The inventors have identified a need for an efficient technique of protecting the passivating layer from chemical interactions between the passivation layer and the electrode comprising aluminum.

PURPOSE OF THE INVENTION

A purpose of the present invention is to provide a new method and a structure for protecting a passivating layer comprising aluminum oxide and being formed on a surface of a silicon substrate from effects caused by chemical interaction between the passivating layer and a conducting electrode. Further, the purpose of the present invention is to provide a new use of the structure.

SUMMARY OF THE INVENTION

The method according to the present invention is characterized by what is presented in independent claim 1.

The structure according to the present invention is characterized by what is presented in independent claim 8.

The use according to the present invention is characterized by what is presented in independent claim 16.

The present invention relates to a method for protecting a passivating layer comprising aluminum oxide and being formed on a surface of a silicon substrate from effects caused by chemical interaction between the passivating layer and a conducting electrode by fabricating a barrier layer between the passivating layer and the conducting electrode, wherein the method comprises depositing a barrier layer comprising titanium and oxygen, tantalum and oxygen, zirconium and oxygen, hafnium and oxygen, or a combination of any of these, or a combination of any of these with aluminum and oxygen, on the passivating layer by exposing the passivating layer in a reaction space to alternately repeated surface reactions of two or more different precursors, wherein at least one of the precursors is a precursor for oxygen; and forming the conducting electrode on the barrier layer deposited on the passivating layer by making a layer comprising aluminum paste on the barrier layer.

The present invention relates further to a structure comprising a barrier layer between a passivating layer and a conducting electrode, wherein the barrier layer is configured to protect the passivating layer comprising aluminum oxide and being formed on a surface of a silicon substrate from effects caused by chemical interaction between the passivating layer and the conducting electrode, wherein the barrier layer comprises titanium and oxygen, tantalum and oxygen, zirconium and oxygen, hafnium and oxygen, or a combination of any of these, or a combination of any of these with aluminum and oxygen, and the conducting electrode comprises a layer comprising aluminum paste. According to one embodiment of the present invention the barrier layer is deposited on the passivating layer by exposing the passivating layer in a reaction space to alternately repeated surface reactions of two or more different precursors, wherein at least one of the precursors is a precursor for oxygen; and the conducting electrode is formed on the barrier layer deposited on the passivating layer by making a layer comprising aluminum paste on the barrier layer.

The aluminum paste used in the present invention can be any aluminum paste usually used for the production of a photovoltaic cell.

The method and the structure of the present invention provide an efficient way of protecting the passivating layer from effects caused by chemical interaction between the passivating layer and the conducting electrode. Surprisingly it was noted that the barrier layer formed by exposing the passivating layer in a reaction space to alternately repeated surface reactions of two or more different precursors efficiently protected the passivating layer by inhibiting chemical reactions from occurring between the passivating layer and the conducting electrode. It was noted that when a barrier layer comprising titanium and oxygen, tantalum and oxygen, zirconium and oxygen, hafnium and oxygen, or a combination of any of these, or a combination of any of these with aluminum and oxygen, was fabricated between the passivating layer and the conducting electrode the harmful effects reducing the passivation property of the passivating layer were significantly reduced compared to an otherwise identical structure without the barrier layer.

In this specification the expression "passivating", "passivation", "surface passivation" or other corresponding expressions should be understood as the passivation of a surface for reducing surface recombination, *i.e.* for reducing the recombination of charge carriers on or in immediate proximity to the passivated surface.

According to the present invention the passivating layer comprises aluminum oxide. According to one embodiment of the present the passivating layer comprises a mixture comprising aluminum oxide.

According to one embodiment of the present invention the barrier layer is deposited on the passivating layer in a reaction space by an atomic layer deposition (ALD) type process.

Atomic Layer Deposition (ALD), or an ALD-type method, is a method for depositing uniform and conformal films, e.g. thin-films, over substrates of various shapes, even over complex 3D (three dimensional) structures. In ALD-type methods the deposit is grown by alternately repeating, essentially self-limiting, surface reactions between a precursor and a surface to be coated. Therefore the growth mechanism in an ALD-type process is commonly not as sensitive as in other coating methods to e.g. the flow dynamics inside a reaction chamber which may be a source for non-uniformity, especially in coating methods relying on gas-phase reactions or in physical deposition methods, such as metal-organic chemical vapor deposition (MOCVD) or physical vapor deposition (PVD).

In an ALD-type process two or more different chemicals (precursors) can be introduced to a reaction space in a sequential, alternating manner and the precursors adsorb on desired surfaces inside the reaction space. The sequential, alternating, introduction of precursors is commonly called pulsing (of precursors). In between each precursor pulse there is commonly a purging period during which a flow of gas which does not react with the precursors used in the process is introduced through the reaction space. This gas, often called the carrier gas is therefore inert towards the precursors used in the process and purges the reaction space from e.g. surplus precursor and by-products resulting from the adsorption reactions of the previous precursor pulse. This purging can be arranged also by other means.

The essential feature of the ALD-type methods is to sequentially expose the deposition surface to precursors and to growth reactions of precursors essentially on the deposition surface. The alternate or sequential exposure of the deposition surface to different precursors can be carried out in different manners. In a batch type ALD process the substrate to be deposited is placed in a reaction space, into which precursor and purge gases are being introduced in a predetermined cycle. In a continuous ALD-type process constant gas flow zones separated in space and a moving substrate are used in order to obtain the time sequential exposure. By moving the substrate through stationary zones, providing precursor exposure and purging areas, in the reaction space, a continuous coating process is achieved enabling roll-to-roll coating of a substrate. In continuous ALD-type process the cycle time depends on the speed of movement of the substrate between the gas flow zones in the reaction space.

The thickness of the deposit, coating or layer produced by the ALD-type process can be increased by repeating several times a pulsing sequence comprising the aforementioned pulses containing the precursor material, and the purging periods. The number of how many times this sequence, called the "ALD cycle", is repeated depends on the targeted thickness of the layer.

The alternate introduction of precursors is characteristic to this deposition process, which is often called atomic layer deposition (ALD). Other names besides ALD have also been employed for these types of processes, where the alternate introduction of two or more different precursors lead to the growth of the layer, often through essentially self-limiting surface reactions. These other names or process variants include atomic layer epotaxy (ALE), atomic layer chemical vapour deposition (ALCVD), and corresponding plasma enhanced variants. Unless otherwise stated, these processes will be collectively addressed as ALD-type processes in this specification.

According to one embodiment of the present invention depositing the barrier layer comprises depositing a layer comprising titanium and oxygen, or a layer comprising tantalum and oxygen. According to one embodiment of the present invention the barrier layer comprises titanium and oxygen, or tantalum and oxygen. According to one embodiment of the present invention depositing the barrier layer comprises depositing a layer comprising an oxide. According to one embodiment of the present invention the barrier layer comprises an oxide. According to one embodiment of the present invention depositing the barrier layer comprises depositing a layer comprising titanium oxide, or tantalum oxide. According to one embodiment of the present invention the barrier layer comprises titanium oxide, or tantalum oxide. According to one embodiment of the present invention depositing the barrier layer comprises depositing a layer comprising a combination of any of the above described materials. According to one embodiment of the present invention the barrier layer comprises a combination of any of the above described materials.

According to one embodiment of the present invention depositing the barrier layer comprises depositing a layer comprising titanium oxide, tantalum oxide, zirconium oxide, hafnium oxide, or a combination of any of these, or a combination of any of these with aluminum oxide. According to one embodiment of the present invention the barrier layer comprises titanium oxide, tantalum oxide, zirconium oxide, hafnium oxide, or a combination of any of these, or a combination of any of these with aluminum oxide.

According to one embodiment of the present invention depositing the barrier layer comprises depositing a layer comprising a nanolaminate structure. According to one embodiment of the present invention the barrier layer comprises a nanolaminate structure.

According to one embodiment of the present invention the nanolaminate structure comprises alternating layers of different oxide materials.

According to one embodiment of the present invention depositing the barrier layer comprises depositing a layer comprising a nanolaminate structure of aluminum oxide and an inert material. According to one embodiment of the present invention the barrier layer comprises a nanolaminate structure of aluminum oxide and an inert material. According to one embodiment of the present invention the inert material is selected from a group consisting of titanium oxide, tantalum oxide, zirconium oxide, and hafnium oxide.

According to one embodiment of the present invention depositing the barrier layer comprises depositing a layer comprising a nanolaminate structure of aluminum oxide and titanium oxide, tantalum oxide, zirconium oxide, or hafnium oxide. According to one embodiment of the present invention the barrier layer comprises a nanolaminate structure of aluminum oxide and titanium oxide, tantalum oxide, zirconium oxide, or hafnium oxide.

According to one embodiment of the present invention the nanolaminate structure is formed with an ALD-type method using an ALD cycle ratio of 2 – 50 cycles for depositing aluminum oxide to 1 – 10 cycles for depositing inert material. According to one embodiment of the present invention the inert material is selected from a group consisting of titanium oxide, tantalum oxide, zirconium oxide, and hafnium oxide.

The surprising barrier effect achieved with the present invention was attributed to the compatibility of the barrier layer between the passivating layer and the conducting electrode. Without limiting the invention to any specific mechanism of why the aforementioned advantage of effective protection was achieved, it is assumed that the barrier layer, comprising titanium and oxygen, tantalum and oxygen, zirconium and oxygen, hafnium and oxygen, or a combination of any of these, or a combination of any of these with aluminum and oxygen, being a stable material, e.g. chemically inert, is able to protect the passivating layer comprising aluminum oxide *e.g.* during the firing step of the manufacturing method of *e.g.* photovoltaic cells. The ALD-type method used for forming the barrier layer between the passivating layer and the conducting electrode provided advantageous properties to the formed barrier layer enabling effective protection of the passivating layer. When the barrier layer is fabricated on the passivating layer by an ALD-type process excellent conformity and uniformity is achieved for the barrier layer. In a similar manner when the passivating layer is fabricated on the surface of the silicon substrate by an ALD-type process excellent conformity and uniformity is achieved for the passivating layer. These advantages of the present invention come in addition to the advantageous protection property of the barrier layer discussed above.

According to one embodiment of the present invention the conducting electrode comprises metal. According to one embodiment of the present invention the conducting electrode comprises aluminum.

According to one embodiment of the present invention depositing the barrier layer is terminated before the barrier layer reaches a thickness of 100 nanometers. According to one embodiment of the present invention the barrier layer has a thickness of below 100 nanometers.

According to one embodiment of the present invention the barrier layer has a thickness of 2 - 50 nanometers, and preferably 1 - 10 nanometers.

According to one embodiment of the present invention the passivating layer has a thickness of 2 - 50 nanometers, and preferably 5 - 10 nanometers.

According to one embodiment of the present invention the passivating layer is formed on the surface of the silicon substrate by depositing the passivating layer on the surface of the silicon substrate in a reaction space by an atomic layer deposition (ALD) type process.

The thickness of the barrier layer can be increased in some embodiments of the present invention by repeatedly exposing the deposition surface to the precursors in the reactions space such that a portion of them adsorbs onto the exposed surfaces in the reaction space *i.e.* onto the deposition surfaces. In this way the protection of the passivating layer may be enhanced in some embodiments of the present invention. In a similar manner also the thickness of the passivating layer can be increased during the ALD-type process.

According to one embodiment of the present invention the silicon substrate is in the form of an electrically conducting layer to an arrangement for a photovoltaic cell.

According to one embodiment of the present invention the growth of the passivating layer and/or the barrier layer in the ALD-type process is essentially thermally activated. *E.g.* the passivation effect is enhanced when the ALD-type process is essentially thermally activated *i.e.* no plasma activation is employed.

The precursors for the deposition process of the barrier layer and/or the passivating layer can be selected from a large group of chemicals. According to one embodiment of the present invention the precursor for titanium is selected from the group of titanium tetrachloride ($TiCl_4$), titanium isopropoxide ($Ti(OCH(CH_3)_2)_4$), titanium ethoxide ($Ti(OCH_2CH_3)_4$), titanium tetramethoxide ($Ti(OCH_3)_4$) and titanium iodide (TiI_4). According to one embodiment of the present invention the precursor for tantalum is selected from the group of tantalum pentachloride ($TaCl_5$), tantalum pentaiodide (TaI_5), tantalum pentaethoxide ($Ta(OEt)_5$), pentakis(dimethylamido)tantalum ($Ta(NMe_2)_5$), and tantalum(V)diethylamide $TA(NEt_2)_5$. According to one embodiment of the present invention the precursor for zirconium is selected from the group of $ZrCl_4$, $ZrCl_2[N(SiMe_3)_2]_2$, ZrI_4, $Zr(OtBu)_4$, $Zr(OtBu)_2(mmp)_2$, $Zr(mmp)_4$, $Zr(ONEt_2)_4$, $Zr(NMe_2)_4$, $Zr(NEt_2)_4$, and $Zr(NEtMe)_4$. According to one embodiment of the present invention the precursor for hafnium is selected from the group of $HfCl_4$, $HfCl_2[N(SiMe_3)_2]_2$, HfI_4, $Hf(OtBu)_4$, $Hf(OtBu)_2(mmp)_2$, $Hf(mmp)_4$, $Hf(ONEt_2)_4$, $Hf(NMe_2)_4$, $Hf(NEt_2)_4$, and $Hf(NEtMe)_4$.

According to one embodiment of the present invention the precursor for aluminum is selected from the group of TMA (trimethylaluminum), TEA (triethylaluminum), $AlCl_3$, $AlBr_3$, $AlMe_2Cl$ $AlMe_2OiPr$, $AlOnPr_3$ and AlOnPr. According to one embodiment of the present invention the precursor for oxygen is selected from the group of H_2O, O_2, O_3, ROHd, $AlOEt_3$, $AlOiOr_3$, H_2O_2, N_2O and N_2O_4. Selecting the other process parameters to deposit the barrier layer and the passivating layer with the selected precursors will be obvious to the skilled person in light of this specification.

According to one embodiment of the present invention the silicon substrate has a thickness of below 200 micrometers.

According to one embodiment of the present invention the method comprises protecting the passivating layer from effects caused by chemical interaction between the passivating layer and the conducting electrode in a photovoltaic cell. According to one embodiment of the present invention the barrier layer is configured to protect the passivating layer from effects caused by chemical interaction between the passivating layer and the conducting electrode in a photovoltaic cell.

The present invention further relates to the use of the structure according to the present invention for protecting a passivating layer comprising aluminum oxide and being formed on a surface of a silicon substrate from effects caused by chemical interaction between the passivating layer and a conducting electrode in a photovoltaic cell.

An advantage of the present invention is that it enables the protection of the passivating layer from being affected by chemicals contained in the back electrode, *i.e.* the layer comprising aluminum paste, which chemicals would cause etching of the passivation layer. The barrier layer according to the present invention prevents etching of the passivating layer, which would lead to at least partial removal of the aluminum oxide and would thus weaken or destroy the surface passivation.

An advantage of the present invention is that the barrier layer fabricated in an ALD-type process and comprising *e.g.* titanium oxide is stable and has the ability to protect the passivating layer comprising aluminum oxide during the firing step of the manufacturing method of the back electrode.

An advantage of the present invention is that both the passivating layer comprising aluminum oxide and the barrier layer can be fabricated in the same ALD-process and apparatus thus removing the need of using any additional deposition equipment.

An advantage of a barrier layer comprising a combination of e.g. two different oxide materials, e.g. a nanolaminate structure, is that a more compact structure can be formed compared to using separate layers or films.

Without limiting the invention to any specific mechanism of why the barrier layer comprising a nanolaminate structure is able to provide effective protection of the passivating layer, it is assumed that the barrier layer having a nanolaminate structure is able to reduce the presence of grain boundaries in the depth direction of the film or layer. The space between grains can be a potential route for traversing the barrier layer. In the nanolaminate structure of two or more oxide materials, the second material will fill the grain boundaries of the material firstly deposited thus hindering unwanted materials from traversing the barrier film.

The embodiments of the invention described hereinbefore may be used in any combination with each other. Several of the embodiments may be combined together to form a further embodiment of the invention. A method, a structure or a use, to which the invention is related, may comprise at least one of the embodiments of the invention described hereinbefore.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are included to provide a further understanding of the invention and constitute a part of this specification, illustrate embodiments of the invention and together with the description help to explain the principles of the invention. In the drawings:

Fig. 1 is a flow-chart illustration of a method according to one embodiment of the present invention, and

Fig. 2 is a schematic illustration of a structure according to one embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Reference will now be made in detail to the embodiments of the present invention, examples of which are illustrated in the accompanying drawings.

For reasons of simplicity, item numbers will be maintained in the following exemplary embodiments in the case of repeating components.

As presented above Atomic Layer Deposition (ALD), or an ALD-type process, is a method for depositing uniform and conformal films or layers over substrates of various shapes. Further, as presented above in ALD-type processes the deposit is grown by alternately repeating, essentially self-limiting, surface reactions between a precursor and a surface to be coated. The prior art discloses a wide range of materials that can be synthesized and deposited on a substrate by alternately exposing the surface of the substrate to different precursors, in an ALD-type process. Also many different apparatuses suitable for carrying out an ALD-type process are disclosed in the prior art. For example US patent 6824816 discloses processes for depositing metal thin-films by ALD, and US patent 6174377 describes deposition tools for ALD.

The construction of a processing tool suitable for carrying out the methods in the following embodiments will be obvious to the skilled person in light of this disclosure. The tool can be *e.g.* a conventional ALD tool suitable for handling the process chemicals. ALD tools (*i.e.* reactors) are disclosed in *e.g.* US patent 4389973 and US patent 4413022 which are included herein as references. Many of the steps related to handling such tools, such as delivering a substrate into the reaction space, pumping the reaction space down to a low pressure, or adjusting gas flows in the tool if the process is done at atmospheric pressure, heating the substrates and the reaction space etc., will be obvious to the skilled person. Also, many other known operations or features are not described here in detail nor mentioned, in order to emphasize relevant aspects of the various embodiments of the invention.

The detailed description below discloses some embodiments of the invention in such a detail that a person skilled in the art is able to utilize the invention based on the disclosure. Not all steps or components of the embodiments are discussed in detail, as many of the steps or components will be obvious to the person skilled in the art based on this specification.

The method of Fig. 1 and the structure of Fig. 2 illustrate, respectively, a method and the corresponding resulting structure according to one embodiment of the invention. The method of Fig. 1 presents how to carry out the method for passivating the silicon substrate 1 with a passivating layer 2 comprising aluminium oxide, and for protecting the passivating layer 2 with a barrier layer 3 against chemical interaction of the passivating layer 2 with the conducting electrode 4 deposited on the other side of the barrier layer 3.

The silicon substrate 1 can be prepared by *e.g.* depositing a film of silicon on a substrate in its microcrystalline, nanocrystalline or polycrystalline phase. The embodiment of Fig. 1 begins by bringing the silicon substrate 1 into the reaction space (step 1)) of a typical reactor tool, *e.g.* a tool suitable for carrying out an ALD-type process.

The reaction space is subsequently pumped down to a pressure suitable for forming the passivating layer 2 comprising aluminum oxide. The reaction space can be pumped down to the suitable pressure using *e.g.* a mechanical vacuum pump or, in the case of atmospheric pressure ALD systems and/or processes, gas flows can be set to protect the deposition zone from the atmosphere. The silicon substrate 1 is also heated to a temperature suitable for forming the passivating layer 2 by the used method. The silicon substrate 1 can be introduced to the reaction space through *e.g.* an airtight load-lock system or simply through a loading hatch. The silicon substrate 1 can be heated by *e.g.* resistive heating elements which also heat the entire reaction space.

After the silicon substrate 1 and the reaction space have reached the targeted temperature and other conditions suitable for deposition, the silicon surface can be conditioned such that the passivating deposit may be essentially directly deposited on the silicon surface. This conditioning of the silicon surface on which the passivating layer 2 is to be deposited can include chemical purification of the surface of the silicon film from impurities and/or oxidation. Especially removal of oxide is beneficial when the silicon surface has been imported into the reaction space via an oxidizing environment, *e.g.* when transporting the exposed silicon surface from one deposition tool to another. The details of the process for removing impurities and/or oxide from the surface of the silicon film will be obvious to the skilled person in view of this specification. In some embodiments of the invention the conditioning can be done ex-situ, *i.e.* outside the tool suitable for ALD-type processes. An example of an ex-situ conditioning process is etching for 1 min in a 1 % HF solution followed by rinsing in DI-water.

After the silicon substrate 1 has been conditioned, an alternate exposure of the deposition surface to different precursor chemicals is started, to form the passivating layer 2 comprising aluminum oxide directly on the silicon substrate 1 (Step a) in Fig. 1). Each exposure of the deposition surface to a precursor results in the formation of additional deposit on the deposition surface, as a result of adsorption reactions of the corresponding precursor with the deposition surface.

A typical reactor suitable for ALD-type deposition comprises a system for introducing carrier gas, such as nitrogen or argon into the reaction space such that the reaction space can be purged from surplus chemical and reaction by-products before introducing the next precursor chemical into the reaction space. This feature together with the controlled dosing of vaporized precursors enables alternately exposing the substrate surface to precursors without significant intermixing of different precursors in the reaction space or in other parts of the reactor. In practice the flow of carrier gas is commonly continuous through the reaction space throughout the deposition process and only the various precursors are alternately introduced to the reaction space with the carrier gas.

Thickness of the passivating layer 2 on the silicon substrate 1 can be controlled by the number of exposures of the deposition surface to the different precursors. The thickness of the passivating layer 2 is increased until a targeted thickness is reached, after which the barrier layer 3 is deposited on the passivating layer 2 (Step b) in Fig. 1).

Deposition of the barrier layer 3, in one embodiment of the invention, is carried out in an ALD-type process in the same deposition tool directly after the deposition of the passivating layer 2 has ended. In this case deposition of the barrier layer 3 can begin simply by changing the precursor chemicals from those used for the deposition of the passivating layer 2 to those suitable for the deposition of the barrier layer 3.

The following example describes in detail how a barrier layer 3 of titanium oxide (TiO_2) can be deposited on the passivating layer 2 residing on the silicon substrate 1.

EXAMPLE

A barrier layer 3 was formed on a passivating layer 2 of aluminum oxide (Al_2O_3) deposited on a surface of a silicon substrate 1; step b) of the embodiment of the invention shown in Fig. 1. The barrier layer 3 was deposited inside the reaction space of a P400 ALD batch tool (available from Beneq OY, Finland) directly after the passivating layer 2 was deposited on the silicon substrate 1 as discussed above. The silicon substrate 1 was a photovoltaic cell structure. This structure was positioned inside the reaction space such that the passivating layer 2 was exposed to the reaction environment.

The pressure and temperature during the deposition of the barrier layer 3 was about 1 mbar (1 hPa) and about 300 °C inside the reaction space, respectively. In this example the carrier gas discussed above, and responsible for purging the reaction space, was nitrogen (N_2). The processing temperature was sufficient to result in a thermally activated ALD-type growth and no plasma activation was employed in this example.

After the passivating layer 2 of aluminum oxide was deposited the precursors were changed to start the deposition of titanium oxide as the barrier layer 3 on the passivating layer 2. Titanium tetrachloride ($TiCl_4$) was introduced to the reaction space to expose the passivating layer 2 to this first precursor. After letting the carrier gas purge the reaction space from surplus first precursor and reaction byproducts, the resulting surface of the substrate was similarly exposed to the second precursor, the precursor for oxygen, here water (H_2O). After this, the reaction space was purged again. This pulsing sequence was carried out once and then repeated 299 times before the process was ended and the substrates were ejected from the reaction space and from the ALD tool. These 300 "ALD cycles" resulted in a barrier layer 3 of titanium oxide with a thickness of approximately 25 nm on the passivating aluminum oxide layer 2.

More specifically, exposure of the surface of the substrate to a specific precursor was carried out by switching on the pulsing valve of the P400 ALD tool controlling the flow of the precursor chemicals into the reaction space. Purging of the reaction space was carried out by closing the valves controlling the flow of precursors into the reaction space, and thereby letting only the continuous flow of carrier gas flow through the reaction space. The pulsing sequence in this example was in detail as follows: 0.6 s exposure to titanium tetrachloride, 1.5 s purge, 0.4 s exposure to water, 2.0 s purge. An exposure time and a purge time in this sequence signify a time a specific pulsing valve for a specific precursor was kept open and a time all the pulsing valves for precursors were kept closed, respectively.

In the example above the first precursor is titanium tetrachloride and the second precursor is water, but other precursors can also be used depending on the desired barrier material and composition. The invention is not limited to using the aforementioned precursors in particular and the advantages of the invention can be obtained by the skilled person in light of this specification also with other precursors.

After the passivating layer 2 and the barrier layer 3 on the passivating layer 2 have been deposited in a single process as described above, the conducting electrode 4, *e.g.* aluminum electrode, is fabricated on the barrier layer 3 to finalize the structure of Fig. 2. The aluminum electrode 4 is then fabricated on the barrier layer 3 by a screen printing method comprising *e.g.* printing the aluminum paste on the barrier layer, drying and curing the paste at high temperature using method steps, which will be obvious to the person skilled in the art.

In the structure of Fig. 2 the barrier layer 3 efficiently protects the underlying passivating layer 2 of aluminum oxide which passivates the surface of the silicon substrate 1 an thereby minimizes surface recombination on the interface between the silicon substrate 1 and the passivating layer 2.

Test results have shown that in the structure of Fig. 2, fabricated with the method of Fig. 1 as described above, the titanium oxide barrier layer 3 protects the aluminum oxide passivating layer 2 especially from chemical interactions with the aluminum electrode 4. This surprisingly enables the passivating layer 2 to retain the passivating effect on the surface of the silicon substrate 1 without significant degradation over time even under challenging environmental conditions such as high temperature. An additional benefit of the method according to the embodiment of Fig. 1 is that, as presented above, the passivating layer 2 and the barrier layer 3 can be fabricated in a single ALD-type process on the silicon substrate 1. The layered structure of Fig. 2 is commonly used in, for example, solar cells and other photovoltaic devices.

In the example above the barrier layer comprises titanium oxide, but the barrier layer could also comprise other materials such as tantalum oxide, zirconium oxide, hafnium oxide, or a combination of any of these, or a combination of any of these with aluminum oxide, as will be obvious to a skilled person in light of this specification. Thus, the invention is not limited to using the aforementioned barrier layer in particular and the advantages of the invention can be readily obtained by the skilled person in light of this specification also with the other materials mentioned above.

It is obvious to a person skilled in the art that with the advancement of technology, the basic idea of the invention may be implemented in various ways. The invention and its embodiments are thus not limited to the examples described above; instead they may vary within the scope of the claims.

CLAIMS

1. A method for protecting a passivating layer (2) comprising aluminum oxide and being formed on a surface of a silicon substrate (1) from effects caused by chemical interaction between the passivating layer and a conducting electrode (4) by fabricating a barrier layer (3) between the passivating layer and the conducting electrode, c h a r a c t e r i z e d in that the method comprises

- depositing a barrier layer (3) comprising titanium and oxygen, tantalum and oxygen, zirconium and oxygen, hafnium and oxygen, or a combination of any of these, or a combination of any of these with aluminum and oxygen, on the passivating layer (2) by exposing the passivating layer in a reaction space to alternately repeated surface reactions of two or more different precursors, wherein at least one of the precursors is a precursor for oxygen; and

- forming the conducting electrode (4) on the barrier layer (3) deposited on the passivating layer by making a layer comprising aluminum paste on the barrier layer.

2. The method of claim 1, c h a r a c t e r i z e d in that the barrier layer (3) is deposited on the passivating layer (2) in a reaction space by an atomic layer deposition (ALD) type process.

3. The method of any one of claims 1 – 2, c h a r a c t e r i z e d in that depositing the barrier layer (3) comprises depositing a layer comprising a nanolaminate structure.

4. The method of any one of claims 1 – 3, c h a r a c t e r i z e d in that depositing the barrier layer (3) is terminated before the barrier layer reaches a thickness of 100 nanometers.

5. The method of any one of claims 1 – 4, c h a r a c t e r i z e d in that the passivating layer (2) is formed on the surface of the silicon substrate

(1) by depositing the passivating layer on the surface of the silicon substrate in a reaction space by an atomic layer deposition (ALD) type process.

6. The method of any one of claims 1 – 5, c h a r a c t e r i z e d in that the silicon substrate (1) is in the form of an electrically conducting layer to an arrangement for a photovoltaic cell.

7. The method of any one of claims 1 – 6, c h a r a c t e r i z e d in that the method comprises protecting the passivating layer (2) from effects caused by chemical interaction between the passivating layer and the conducting electrode (4) in a photovoltaic cell.

8. A structure comprising a barrier layer (3) between a passivating layer (2) and a conducting electrode (4), wherein the barrier layer is configured to protect the passivating layer comprising aluminum oxide and being formed on a surface of a silicon substrate (1) from effects caused by chemical interaction between the passivating layer and the conducting electrode, c h a r a c t e r i z e d in that the barrier layer (3) comprises titanium and oxygen, tantalum and oxygen, zirconium and oxygen, hafnium and oxygen, or a combination of any of these, or a combination of any of these with aluminum and oxygen, and the conducting electrode (4) comprises a layer comprising aluminum paste.

9. A structure of claim 8, c h a r a c t e r i z e d in that the barrier layer (3) is deposited on the passivating layer (2) by exposing the passivating layer in a reaction space to alternately repeated surface reactions of two or more different precursors, wherein at least one of the precursors is a precursor for oxygen; and the conducting electrode (4) is formed on the barrier layer deposited on the passivating layer by making a layer comprising aluminum paste on the barrier layer.

10. The structure of any one of claims 8 - 9, c h a r a c t e r i z e d in that the barrier layer (3) is deposited on the passivating layer (2) in a reaction space by an atomic layer deposition (ALD) type process.

11. The structure of any one of claims 8 – 10, c h a r a c t e r i z e d in that the barrier layer (3) comprises a nanolaminate structure.

12. The structure of any one of claims 8 – 11, c h a r a c t e r i z e d in that the barrier layer (3) has a thickness of below 100 nanometers.

13. The structure of any one of claims 8 – 12, c h a r a c t e r i z e d in that the passivating layer (2) is formed on the surface of the silicon substrate (1) by depositing the passivating layer on the surface of the silicon substrate in a reaction space by an atomic layer deposition (ALD) type process.

14. The structure of any one of claims 8 – 13, c h a r a c t e r i z e d in that the silicon substrate (1) is in the form of an electrically conducting layer to an arrangement for a photovoltaic cell.

15. The structure of any one of claims 8 – 14, c h a r a c t e r i z e d in that the barrier layer (3) is configured to protect the passivating layer (2) from effects caused by chemical interaction between the passivating layer and the conducting electrode (4) in a photovoltaic cell.

16. The use of a structure of any one of claims 8 – 15 for protecting a passivating layer (2) comprising aluminum oxide and being formed on a surface of a silicon substrate (1) from effects caused by chemical interaction between the passivating layer (2) and a conducting electrode (4) in a photovoltaic cell.

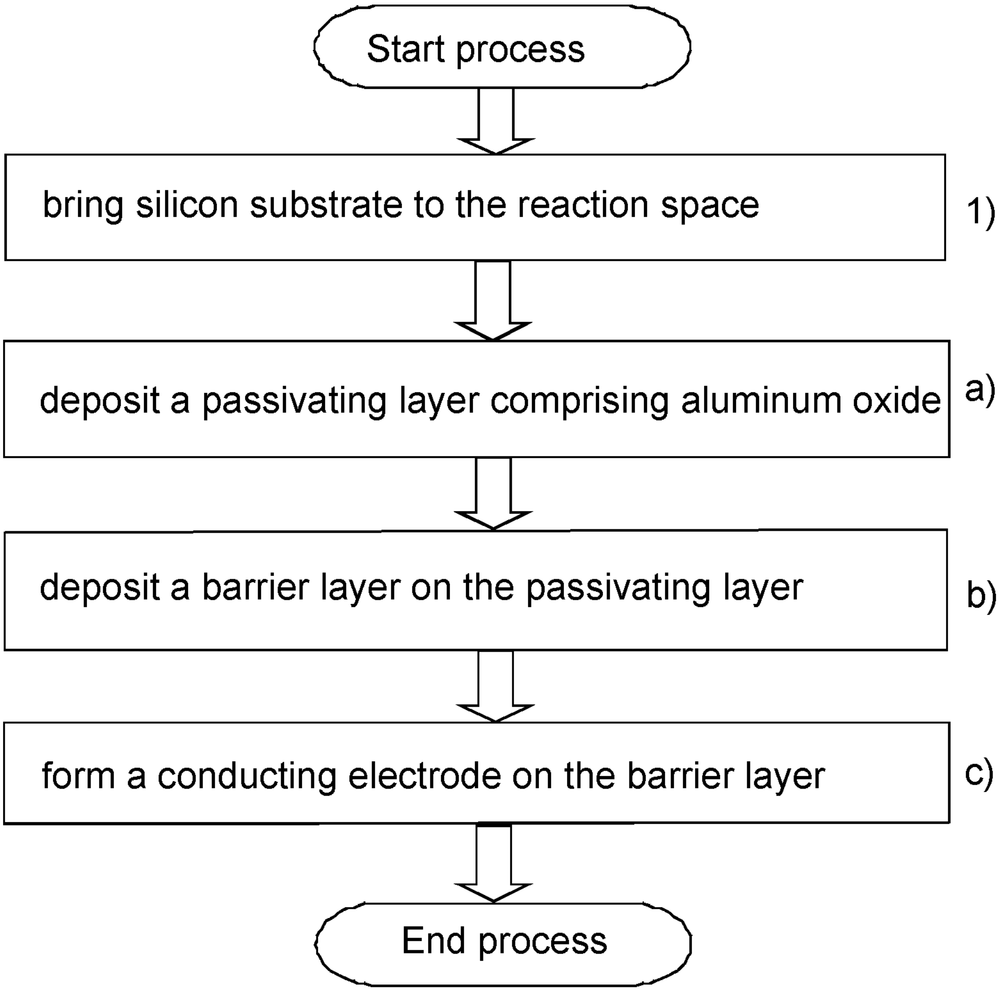
Start process
bring silicon substrate to the reaction space
1)
deposit a passivating layer comprising aluminum oxide
a)
deposit a barrier layer on the passivating layer
b)
form a conducting electrode on the barrier layer
c)
End process

Fig. 1

Fig. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2012/050514

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

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)

IPC: C23C, H01L

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

FI, SE, NO, DK

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI, XPIEE, XPESP, XPI3E, XPAIP

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 2312650 A2 (IPS LTD) 20 April 2011 (20.04.2011) paragraphs [0010]-[0011],[0017]-[0019] and [0023]-[0026]	1-16
Y	SAINT-CAST, P. et al. High-Efficiency c-Si Solar Cells Passivated With ALD and PECVD Aluminum Oxide. IEEE electr. lett. July 2010, vol. 31, no 7, p.695-697. section II	1-16
Y	SCHMIDT, J. et al. Silicon surface passivation by ultrathin Al2O3 films and Al2O3/SiNx stacks. In: Conference Proceedings, 35th IEEE Photovoltaic Specialists Conference (PVSC), 20.-25.6.2010, Honolulu, USA, p.885-890 section "PERC solar cells" on page 889	1-16
Y	SCHMIDT, J. et al. Surface passivation of high-efficiency silicon solar cells by atomic-layer-deposited Al2O3. Prog. photovolt: res. appl., september 2008, vol. 16, no 6, p.461-466. abstract, figure 2	1-16

☒ Further documents are listed in the continuation of Box C. ☒ 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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 September 2012 (24.09.2012)	26 September 2012 (26.09.2012)

Name and mailing address of the ISA/FI	Authorized officer
National Board of Patents and Registration of Finland P.O. Box 1160, FI-00101 HELSINKI, Finland Facsimile No. +358 9 6939 5328	Thomas Carlsson Telephone No. +358 9 6939 500

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 1635398 A2 (UNIV NORTH CAROLINA STATE) 15 March 2006 (15.03.2006) paragraphs [0011],[0035],[0044]-[0045],[0050] and [0057]-[0060]	1-16
A	US 2010263725 A1 (SCHMIDT JAN) 21 October 2010 (21.10.2010)	
A	DINGEMANS, G. et al. Recent Progress in the Development and Understanding of Silicon Surface Passivation by Aluminum Oxide for Photovoltaics. In: EU PVSEC Proceedings, 25th European Photovoltaic Solar Energy Conference and Exhibition / 5th World Conference on Photovoltaic Energy Conversion, 6.-10.9.2010, Valencia, Spain, p. 1083-1090.	
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/FI2012/050514

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EP 1635398 A2	15/03/2006	US 2006054937 A1	16/03/2006
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INTERNATIONAL SEARCH REPORT

International application No.
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CLASSIFICATION OF SUBJECT MATTER

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C23C 16/455 (2006.01)
H01L 31/18 (2006.01)
H01L 31/0216 (2006.01)
H01L 21/02 (2006.01)