

**IN THE UNITED STATES DISTRICT COURT
FOR THE DISTRICT OF DELAWARE**

HANWHA Q CELLS & ADVANCED
MATERIALS CORPORATION,

Plaintiff,

v.

REC SOLAR HOLDINGS AS,
REC SOLAR PTE. LTD., AND
REC AMERICAS, LLC

Defendants.

Civil Action No. _____

DEMAND FOR JURY TRIAL

COMPLAINT FOR PATENT INFRINGEMENT

Plaintiff Hanwha Q CELLS & Advanced Materials Corporation (“Hanwha Q CELLS” or “Plaintiff”) files this Complaint for patent infringement against Defendants REC Solar Holdings AS, REC Solar Pte. Ltd., and REC Americas, LLC (collectively, “REC,” “REC Defendants,” or “Defendants”), and alleges as follows:

NATURE OF THE ACTION

1. This action is brought against REC Defendants for infringement of U.S. Patent No. 9,893,215 (the “’215 Patent”), which is directed to solar cells. Hanwha Q CELLS is the sole owner by assignment of all right, title, and interest in the ’215 Patent, including the right to recover damages for past infringement.

2. A true and correct copy of the ’215 Patent is attached as Exhibit 1.

THE PARTIES

3. Plaintiff Hanwha Q CELLS & Advanced Materials Corporation is a corporation organized under the laws of the Republic of Korea with an address at 86 Cheonggyecheon-ro, Jung-gu, Seoul, Republic of Korea 04541.

4. Hanwha Q CELLS is one of the largest photovoltaic solar cell and solar module manufacturers in the world. Through its research and development facility, Hanwha Q CELLS has pioneered applications of solar cell technology that achieves higher energy conversion efficiency than traditional solar cells.

5. Defendant REC Solar Holdings AS (“REC Holdings”) is a Norwegian corporation with an address at Drammensveien 169, Oslo, 0277, Norway. REC Holdings has subsidiary and/or affiliate corporations in locations including Singapore, Germany, Japan, India, and the United States.

6. Defendant REC Solar Pte. Ltd. (“REC Pte”) is a Singaporean corporation with an address at 20 Tuas South Ave. 14, Tuas, 637312, Singapore. Upon information and belief, REC Pte is one of REC Holdings’ subsidiaries and/or affiliates.

7. Defendant REC Americas LLC (“REC Americas”) is a Delaware corporation that is, upon information and belief, one of REC Holdings’ subsidiaries and/or affiliates. Upon information and belief, REC Americas has an address at 1820 Gateway Drive, Suite 170, San Mateo, California 94404. Upon information and belief, REC Americas offers for sale and sells REC’s solar modules for solar projects throughout the United States.

JURISDICTION AND VENUE

8. This is an action for patent infringement under the patent laws of the United States of America, 35 U.S.C. §§ 1, *et seq.*, including 35 U.S.C. §§ 271 and 281–85. This Court therefore has subject matter jurisdiction over this action pursuant to 28 U.S.C. §§ 1331 and 1338.

9. This Court has personal jurisdiction over each of the Defendants.

10. Defendant REC Americas is a Delaware corporation. Thus, REC Americas resides within, and has consented to, personal jurisdiction within the District of Delaware.

11. Defendant REC Holdings has conducted and continues to conduct business in the State of Delaware and in the District of Delaware. REC Holdings, upon information and belief, directly and/or through its subsidiaries, makes or assembles products that are covered by the subject matter of the '215 Patent and that are and have been imported, offered for sale, sold, purchased, and used within the District of Delaware. REC Holdings, upon information and belief, directly or through intermediaries (including subsidiaries, distributors, retailers, contractors, and others), purposefully and voluntarily ships, distributes, offers for sale, sells, installs, uses, and advertises infringing products to consumers in the District of Delaware. Additionally, REC Holdings, directly and/or through distribution networks, regularly places infringing products within the stream of commerce, with the knowledge and/or understanding that such products will be sold in the District of Delaware. Upon information and belief, REC Holdings has committed acts of patent infringement within the State of Delaware and in the District of Delaware. REC Holdings has purposefully availed itself of the benefits of the State of Delaware and the exercise of jurisdiction over REC Holdings would not offend traditional notions of fair play and substantial justice.

12. Defendant REC Pte, upon information and belief, directly and/or through their subsidiaries or affiliates, makes or assembles products that are covered by the subject matter of the '215 Patent and that are and have been imported, offered for sale, sold, purchased, and used within the District of Delaware. REC Pte, upon information and belief, directly and/or through intermediaries (including subsidiaries, affiliates, distributors, retailers, contractors, and others), including distribution networks controlled by affiliated entities, regularly places infringing products within the stream of commerce, with the knowledge and/or understanding that such products are shipped, distributed, offered for sale, sold, installed, used, and advertised to

consumers within the District of Delaware. REC Pte has committed acts of patent infringement within the State of Delaware and in the District of Delaware. REC Pte has purposefully availed itself of the benefits of the State of Delaware and the exercise of jurisdiction over REC Pte would not offend traditional notions of fair play and substantial justice.

13. In the event that this Court does not have personal jurisdiction over Defendants REC Holdings and REC Pte by virtue of the above, this Court nonetheless has personal jurisdiction over those Defendants pursuant to Federal Rule of Civil Procedure 4(k)(2) because this case arises under federal law, REC Holdings and REC Pte are not subject to jurisdiction in any state's courts of general jurisdiction, and REC Holdings and REC Pte have purposefully availed themselves of the privilege of conducting business in the United States by making, using, offering to sell, or selling infringing products within the United States, or importing infringing products into the United States.

14. Venue is proper in this District for Defendant REC Americas under 28 U.S.C. §§ 1391(b) and (c) and 28 U.S.C. § 1400 because, among other reasons, REC Americas is subject to personal jurisdiction in the District of Delaware and reside in the District of Delaware.

15. Venue is proper in this District for Defendants REC Holdings and REC Pte under 28 U.S.C. § 1391(c) because, among other reasons, those Defendants are subject to personal jurisdiction and are not resident in the United States.

THE PATENTED INVENTION

16. Hanwha Q CELLS incorporates the allegations of the preceding paragraphs as if fully set forth herein.

17. The '215 Patent is entitled "Method for Manufacturing a Solar Cell with a Surface-Passivating Dielectric Double Layer, and Corresponding Solar Cell." The '215 Patent issued from U.S. Patent Application Serial No. 12/742,818 (the "'818 Application"). The '818

Application is a national stage application of PCT/EP2008/065067, with a 35 U.S.C. § 371(c) date of July 2, 2010 and claims the benefit of German Patent Application Serial No. 10 2007 054 384.2, filed on November 14, 2007. The '215 Patent identifies Jan Schmidt and Bram Hoex as the inventors.

18. The technology claimed in the '215 Patent concerns solar cells, which are semiconductor devices that utilize the photovoltaic effect to convert sunlight (i.e., photons) into electricity. '215 Patent, col. 3:7–20, Ex. 1. The photovoltaic effect refers to the generation of energy-containing charge carriers when a material, such as silicon, is exposed to sunlight. Sunlight exposure creates negative and positive charge carriers within a silicon substrate. *See id.*, col. 1:16–22. The energy contained in these charge carriers must be extracted and utilized externally without the charge carriers recombining at the boundary surface of the silicon substrate and neutralize each other, a process known as recombination. *See id.*, col. 1:14–22.

19. The '215 Patent discloses a structure of solar cells with certain efficiency advantages versus other types of solar cells. *See id.*, col. 6:8–34. The solar cell structure of the '215 Patent includes a silicon substrate, a first dielectric layer comprising aluminum oxide on a surface of the silicon substrate, and a second dielectric layer on the first dielectric layer of different materials and with hydrogen being embedded into the second dielectric layer. *Id.*, col. 5:58–64.

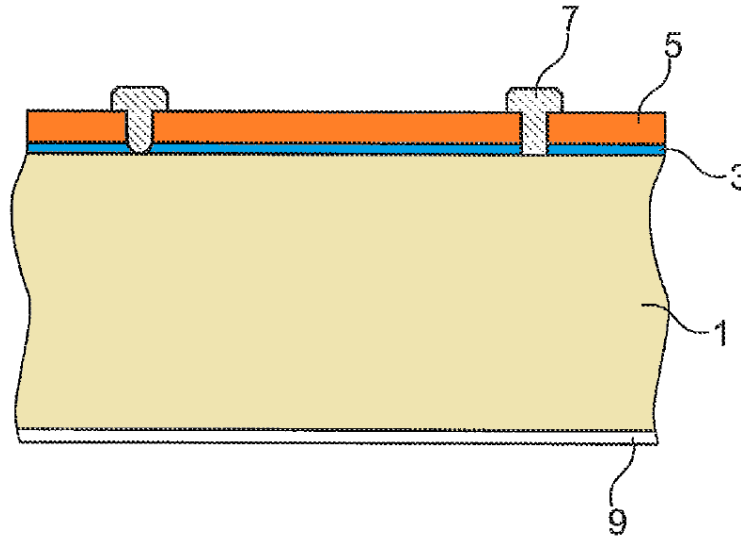


Figure 1

20. Figure 1 (above and colored) from the '215 Patent shows an exemplary illustration depicting the first and second dielectric layers on a silicon substrate (1). The first dielectric layer comprising aluminum oxide (3) is deposited on a surface of the silicon substrate, and the second dielectric layer (5) is deposited on top of the first dielectric layer. *Id.*, col. 7:30–35. The second dielectric layer has hydrogen embedded within the layer. *Id.*, col. 7:65–8:3.

21. The use of these surface-passivating dielectric layers reduces surface recombination of charge carriers, allowing greater extraction of energy-containing charge carriers for external utilization. *Id.*, col. 2:58–60, 3:1–4. The use of the surface-passivating dielectric layers may increase light absorption in the substrate, and increase the efficiency of light conversion into electricity. *Id.*, col. 3:7–20. Further, the solar cells with the disclosed structure maintain their stable passivation properties while withstanding the high temperatures used in today's industrial manufacturing processes. *Id.*, col. 3:4–7. As a result, the invention of the '215 Patent allows more energy to be extracted from the solar cell, while remaining durable through the manufacturing process. *Id.*, col. 3:4–27.

CLAIMS FOR PATENT INFRINGEMENT

Count I: Infringement of U.S. Patent No. 9,893,215

22. Hanwha Q CELLS incorporates the allegations of the preceding paragraphs as if fully set forth herein.

23. REC Defendants are in the business of designing, manufacturing, using, offering to sell, selling, and importing products, including solar cells and modules, both under the REC brand and, upon information and belief, as a contract manufacturer for other companies.

24. Hanwha Q CELLS is informed and believes, and thereon alleges, that REC has infringed, is currently infringing, or will infringe the '215 Patent in violation of 35 U.S.C. § 271 by, among other things, making, using, offering to sell, or selling, within the United States, or importing into the United States, without license or authority, products—including solar cells and solar modules—that infringe the '215 Patent (the “Accused Products”), literally or under the doctrine of equivalents.

25. Upon information and belief, REC manufactures solar cells and incorporate those cells into REC-branded solar modules at REC’s factory or factories in Singapore. Upon information and belief, REC Pte operates such a factory located in Singapore. REC, including through REC Americas, offers for sale and sells the aforementioned solar products to customers within the United States. Upon information and belief, REC has entered into business agreements that depend on its importation of infringing solar cells and/or modules. Upon information and belief, REC has sold over 2.2 gigawatts of its solar modules, with approximately forty percent of these sales to the United States. Upon information and belief, REC sold 200 megawatts of its solar modules in December 2018 for installations and solar projects across the United States. REC has installed its solar modules in a number of solar installations throughout the United States, including in San Rafael, California; Fresno, California; Kaua’i, Hawaii;

Sandy, Utah; Sweetwater, Florida; Indianapolis, Indiana; Pacific Palisades, California; Tucson, Arizona; Madera, California; Morrisville, North Carolina, and Siler City, North Carolina.

26. Based on the information presently available to it, Hanwha Q CELLS alleges that REC's Accused Products include, but are not limited to, the following solar modules: REC265TP; REC270TP; REC275TP; REC280TP; REC285TP; REC265TP BLK; REC270TP BLK; REC275TP BLK; REC280TP BLK; REC285TP BLK; REC275TP2; REC280TP2; REC285TP2; REC290TP2; REC295TP2; REC300TP2; REC275TP2 BLK2; REC280TP2 BLK2; REC285TP2 BLK2; REC300TP2M; REC305TP2M; REC310TP2M; REC315TP2M; REC320TP2M; REC330TP2S72; REC335TP2S72; REC340TP2S72; REC345TP2S72; REC350TP2S72; REC355TP2S72; REC360TP2SM72; REC365TP2SM72; REC370TP2SM72; REC375TP2SM72; REC380TP2SM72. Hanwha Q CELLS further alleges that the Accused Products are manufactured in REC's factory or factories including at least one operated by REC Pte.

27. As an exemplary infringing product, REC REC285TP2 BLK2 can be purchased within the United States and contains one hundred twenty individual solar cells. Upon information and belief, the REC REC285TP2 BLK2 solar module includes solar cells that infringe at least claims 12–14 of the '215 Patent. For example, REC REC285TP2 BLK2 contains each element of and infringes at least claim 12 of the '215 Patent, which recites the following:

12. A solar cell comprising:
 - a silicon substrate;
 - a first dielectric layer comprising aluminium oxide on a surface of the silicon substrate; and
 - a second dielectric layer directly on a surface of the first dielectric layer, materials of the first dielectric layer and the second dielectric layer differing and hydrogen being embedded into the second dielectric layer;

wherein the first dielectric layer has a thickness of less than 50 nm and is interposed between the surface of the silicon substrate and the second dielectric layer.

28. Specifically, the REC REC285TP2 BLK2 solar module is comprised of a silicon substrate and a stack of layers, including a first dielectric layer, and a second dielectric layer. The materials of the first and second dielectric layers differ. The first dielectric layer comprises aluminum oxide, and the second dielectric layer includes the elements silicon and nitrogen. The first dielectric layer is less than 50 nanometers thick. The second dielectric layer contains hydrogen. The first dielectric layer is interposed between the second dielectric layer and the surface of the silicon substrate.

29. A cross-sectional measurement mapping of the backside edge of a sample piece extracted from a representative solar cell in a REC REC285TP2 BLK2 module indicates that the solar cell comprises a silicon substrate, followed by a first dielectric layer including the elements of aluminum and oxygen, which is followed by a second dielectric layer of different materials than the layer including aluminum and oxygen.

30. A depth profile measurement on a sample prepared from a representative solar cell contained in a REC REC285TP2 BLK2 module shows that elements of aluminum and oxygen are present inside a 50-nanometer band, indicating a first dielectric layer comprising aluminum oxide of a thickness less than 50 nanometers.

31. A depth profile measurement on a sample prepared from a representative solar cell contained in a REC REC285TP2 BLK2 module shows the presence of hydrogen in the second dielectric layer, indicating that hydrogen is embedded into the second dielectric layer.

32. Upon information and belief, the exemplary REC REC285TP2 BLK2 solar module is representative of many other products that are made, used, offered for sale, or sold, within the United States, or imported into the United States, by or on behalf of REC, and that

present the same or substantially similar features as the exemplary REC REC285TP2 BLK2 solar module. Accordingly, on information and belief, Hanwha Q CELLS alleges that numerous REC products including the exemplary REC REC285TP2 BLK2 infringe at least claims 12–14 of the '215 Patent and have been made, used, offered for sale, or sold within the United States, or imported into the United States, by or on behalf of REC.

33. Hanwha Q CELLS anticipates that discovery will further confirm the full scope of infringing products that are made, used, offered for sale, or sold, within the United States, or imported into the United States, by or on behalf of REC. Hanwha Q CELLS makes the preliminary identification of the Accused Products without the benefit of discovery or claim construction in this action, and expressly reserves the right to augment, supplement, and revise its identifications based on additional information obtained through discovery or otherwise.

34. REC has had knowledge of the '215 Patent since before this Complaint was filed, or at a minimum will receive notice of the '215 Patent upon filing of the Complaint.

35. REC's acts of infringement have caused damage to Hanwha Q CELLS in an amount yet to be determined and subject to proof at trial.

PRAYER FOR RELIEF

WHEREFORE, Hanwha Q CELLS prays for relief as follows:

A. Judgment that REC Defendants have directly infringed the '215 Patent, both literally and under the doctrine of equivalents;

B. REC Defendants be ordered to account for and compensate Plaintiff Hanwha Q CELLS for REC Defendants' infringing activities, including supplemental damages for any post-verdict infringement up until entry of the final judgment with an accounting as needed, together with pre-judgment and post-judgment interest on the damages awarded;

C. An award of enhanced damages under 35 U.S.C. § 284 to the extent that the Court deems appropriate;

D. An award of reasonable attorney fees pursuant to 35 U.S.C. § 285 to the extent that the Court deems this case is an exceptional case;

E. Injunctive relief in that REC Defendants, their affiliates, subsidiaries, officers, agents, servants, employees, and successors and assigns, and other persons who are in active concert or participation with anyone in the foregoing, be preliminarily and permanently enjoined from infringement of the '215 Patent, including but not limited to an injunction against making, using, offering to sell, selling within the United States, and importing into the United States, products that infringes the '215 Patent;

F. Costs of suit incurred herein; and

G. Any and all other relief that the Court deems just and equitable.

DEMAND FOR JURY TRIAL

Hanwha Q CELLS hereby demands a trial by jury on all issues.

Dated: March 5, 2019

Respectfully submitted,

Of Counsel:

YOUNG CONAWAY
STARGATT & TAYLOR, LLP

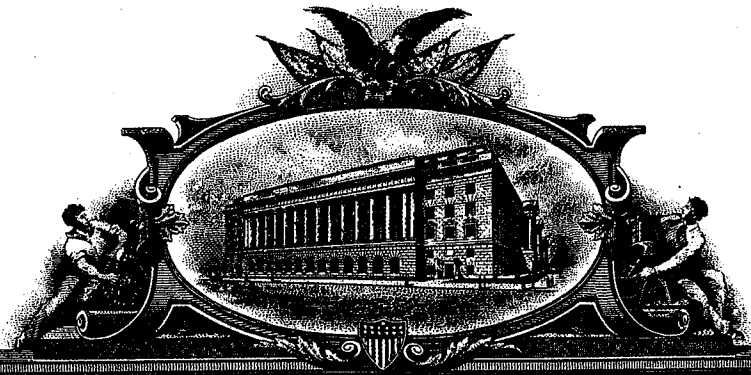
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EXHIBIT 1



U 7705112

THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME;

**UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office**

December 19, 2018

**THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM
THE RECORDS OF THIS OFFICE OF:**

**U.S. PATENT: 9,893,215
ISSUE DATE: February 13, 2018**

**By Authority of the
Under Secretary of Commerce for Intellectual Property
and Director of the United States Patent and Trademark Office**

**P. SWAIN
Certifying Officer**





US009893215B2

(12) **United States Patent**
Schmidt et al.

(10) **Patent No.:** **US 9,893,215 B2**
(45) **Date of Patent:** **Feb. 13, 2018**

(54) **METHOD FOR MANUFACTURING A SOLAR CELL WITH A SURFACE-PASSIVATING DIELECTRIC DOUBLE LAYER, AND CORRESPONDING SOLAR CELL**

(58) **Field of Classification Search**
CPC H01L 31/00; H01L 27/00; H01L 31/0256; H01L 31/18; H01L 31/02168
(Continued)

(75) **Inventors:** **Jan Schmidt**, Hameln (DE); **Bram Hoex**, Singapore (SG)

(56) **References Cited**

(73) **Assignees:** **HANWHA Q CELLS CO., LTD**, Grand Cayman (KY); **SOLARWORLD INDUSTRIES GMBH**, Bonn (DE)

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(Continued)

(*) **Notice:** Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 1007 days.

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(Continued)

(21) **Appl. No.:** **12/742,818**

(22) **PCT Filed:** **Nov. 6, 2008**

(86) **PCT No.:** **PCT/EP2008/065067**

§ 371 (c)(1),
(2), (4) **Date:** **Jul. 2, 2010**

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(Continued)

(87) **PCT Pub. No.:** **WO2009/062882**

PCT Pub. Date: **May 22, 2009**

(65) **Prior Publication Data**

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Primary Examiner — Tae-Sik Kang

(74) *Attorney, Agent, or Firm* — Birch, Stewart, Kolasch & Birch, LLP

(30) **Foreign Application Priority Data**

Nov. 14, 2007 (DE) 10 2007 054 384

(57) **ABSTRACT**

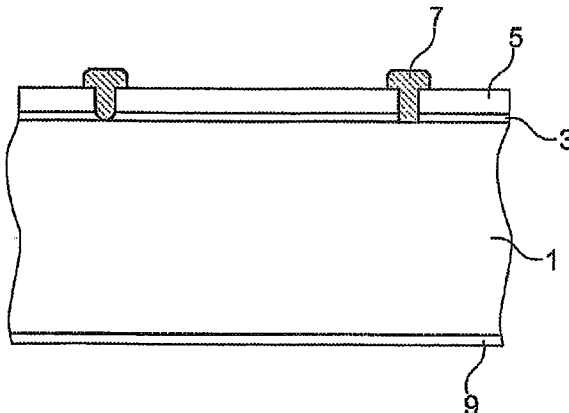
A solar cell with a dielectric double layer and also a method for the manufacture thereof are described. A first dielectric layer (3), which contains aluminum oxide or consists of aluminum oxide, and a second, hydrogen-containing dielectric layer (5) are produced by means of atomic layer deposition, allowing very good passivation of the surface of solar cells to be achieved.

(51) **Int. Cl.**
H01L 31/18 (2006.01)
H01L 31/0256 (2006.01)

(Continued)

(52) **U.S. Cl.**
CPC **H01L 31/02168** (2013.01); **C23C 16/403** (2013.01); **C23C 16/45542** (2013.01); **Y02E 10/50** (2013.01)

16 Claims, 1 Drawing Sheet



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Page 2

- (51) **Int. Cl.**
H01L 31/0216 (2014.01)
C23C 16/40 (2006.01)
C23C 16/455 (2006.01)
- (58) **Field of Classification Search**
USPC 136/261
See application file for complete search history.

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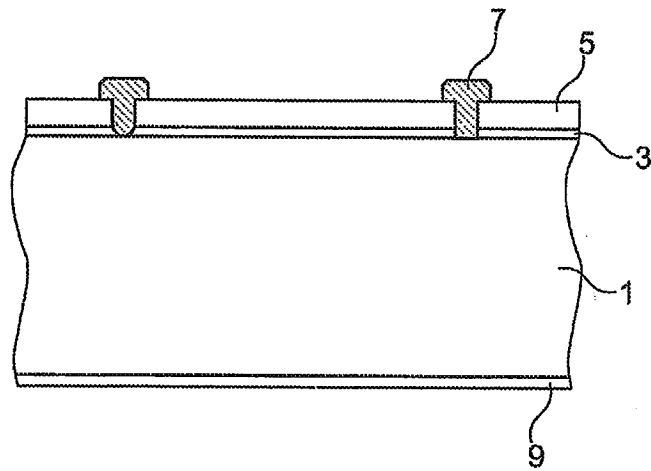
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U.S. Patent

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METHOD FOR MANUFACTURING A SOLAR CELL WITH A SURFACE-PASSIVATING DIELECTRIC DOUBLE LAYER, AND CORRESPONDING SOLAR CELL

FIELD OF THE INVENTION

The present invention relates to a method for manufacturing a solar cell with a surface-passivating dielectric double layer and to a corresponding solar cell.

BACKGROUND OF THE INVENTION

A key requirement for achieving high degrees of efficiency in solar cells is very effective suppression of surface recombination losses. For this purpose, the surface of solar cells should be passivated as effectively as possible, so that charge carrier pairs which are generated inside the solar cell by incident light and which diffuse to the surfaces of the solar cell substrate do not recombine at the solar cell surface, so that they would no longer be available to help improve the efficiency of the solar cell.

In laboratory solar cells, this problem is often solved by growing silicon dioxide at a high temperature (for example >900° C.). However, as a high-temperature process step of this type means considerable additional expenditure in solar cell processing, surface passivation of this type is at present generally not used in the industrial manufacture of solar cells.

A further difficulty of high-temperature oxidation is the sensitivity of more economical multicrystalline silicon in relation to high temperatures which can lead in this material to a considerable reduction in material quality, i.e. the charge carrier lifetime, and thus to losses in efficiency.

A low-temperature alternative is surface passivation using amorphous silicon nitride or silicon carbide which can be prepared at temperatures of 300-400° C. by means of plasma enhanced chemical vapour deposition (PECVD), for example. Surface passivation of this type is for example described in T. Lauinger et al.: "Record low surface recombination velocities on 1 □cm p-silicon using remote plasma silicon nitride passivation", Appl. Phys. Lett. 68, 1232-1234 (1996); and in I. Martin et al.: "Surface passivation of p-type crystalline silicon by plasma enhanced chemical vapor deposited amorphous SiC_x films", Appl. Phys. Lett. 79, 2199-2201 (2001). However, the dielectric layers produced in this way can be used only to a limited degree for large-area, high-efficiency solar cells, as they can contain a high density of what are known as "pinholes", i.e. small holes or pores in the layer, so that they may not have good insulating properties. In addition, their passivating effect is based largely on a very high positive charge density within the dielectric layers that can lead, during the passivation of the back of the solar cell if p-type silicon wafers are used, for example, to the formation of an inversion layer via which an additional leakage current of minority charge carriers can flow away from the base of the solar cell to the back contacts (what is known as a "parasitic shunt"). On highly boron-doped p⁺ silicon surfaces, silicon nitride can even lead, on account of the high positive charge density, to depassivation compared to an unpassivated p⁺ surface.

Very good passivations, both on p and on p⁺ surfaces, were achieved using amorphous silicon layers which can also be produced by means of plasma enhanced vapour deposition at very low coating temperatures (typically <250° C.), such as is described for example in S. Dauwe et al.: "Very low surface recombination velocities on p- and n-type

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silicon wafers passivated with hydrogenated amorphous silicon films", Proc. 29th IEEE Photovoltaic Specialists Conf., New Orleans, USA (2002), p. 1246; and in P. Altermatt et al.: "The surface recombination velocity at boron-doped emitters: comparison between various passivation techniques", Proceeding of the 21st European Photovoltaic Solar Energy Conference, Dresden (2006), p. 647.

However, the surface-passivating property of amorphous silicon layers of this type may be very susceptible to temperature treatments. In current-day industrial solar cell processes, the metal coating is in many cases carried out by means of screen printing technology, the last process step typically being a firing of the contacts in a continuous infrared furnace at temperatures between approx. 800° C. and 900° C. Although the solar cell is exposed to these high temperatures only for a few seconds, this firing step can lead to considerable degradation of the passivating effect of the amorphous silicon layers.

Good passivating results can also be achieved using aluminium oxide layers which are deposited by means of atomic layer deposition (ALD) at about 200° C., for example, and subsequently tempered at about 425° C. Nevertheless, in atomic layer deposition, only a single molecular layer of the material to be deposited is generally deposited on the substrate surface within each deposition cycle. As a deposition cycle typically lasts about 0.5 to 4 s, correspondingly low deposition rates are obtained. The deposition of aluminium oxide layers at a thickness which is suitable for use as an antireflection layer or as a back reflector therefore requires deposition durations which have in the past shown a use of such layers in industrially produced solar cells to be commercially disadvantageous.

SUMMARY OF THE INVENTION

There may be a need for a solar cell and for a method for manufacturing a solar cell in which, on the one hand, good passivation of the surface of the solar cell can be achieved and, on the other hand, the above-mentioned drawbacks of conventional surface-passivating layers can be at least partially avoided. In particular, it should be possible to produce solar cells displaying very good surface passivation in an economical, industrially viable manner.

This need can be met by the subject matter of the independent claims. Advantageous embodiments of the present invention are described in the dependent claims.

According to a first aspect of the present invention, a method is proposed for manufacturing a silicon solar cell, including the following steps: providing a silicon substrate; depositing a first dielectric layer on a surface of the silicon substrate by means of atomic layer deposition, wherein the first dielectric layer comprises aluminium oxide; and depositing a second dielectric layer on a surface of the first dielectric layer, the materials of the first and the second dielectric layer differing and hydrogen being embedded into the second dielectric layer.

This first aspect of the present invention may be regarded as being based on the following idea: a method is specified for manufacturing silicon solar cells with a dielectric passivating layer for reducing surface recombination losses. The dielectric passivating layer is composed of two partial layers, of a very thin aluminium oxide-containing layer, which is formed by atomic layer deposition (ALD), and also of a thicker layer made of silicon oxide, silicon nitride or silicon carbide, for example, which can be deposited on the aluminium oxide layer by means of plasma enhanced chemical vapour deposition (PECVD), for example.

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The dielectric double layer produced in the method according to the first aspect allows the passivation of both high and low-doped regions of the solar cell surface of conduction type p or n. It is possible to allow stable passivation which retains its passivating properties even after a firing step in the temperature range of 800-900° C. for burning-in of metal contacts. At the same time, the dielectric passivating layer can also have advantageous optical properties, i.e. for application to the front of the solar cell, the layer can serve as an effective antireflection layer; during application to the back of the solar cell, the passivating layer can form, together with metal coating over the entire area of the back, an effective mirror for photons with energies close to the silicon band gap in order to improve what is known as "light trapping", i.e. the trapping of light by multiple internal reflection, in the solar cell. Furthermore, the negative effect of "parasitic shunting", which is known from silicon nitride, can be avoided for rear surface passivation on standard solar cell semiconductor material of conduction type p.

The key to understanding the outstanding passivating effect and tempering stability of the stack layer according to the invention may be identified in the combination of the Si/Al₂O₃ interface, which is ideally atomically flat and is produced as a matter of course during the ALD process, and the highly hydrogenous SiO₂, SiN_x or SiC_x layers, such as are formed during the PECVD process, for example. A part of the hydrogen from the PECVD-deposited layers can diffuse through the ultrathin Al₂O₃ layer and passivate unsaturated silicon bonds at the interface to the silicon.

Features, details and possible advantages of embodiments of the manufacturing method according to the invention will be described hereinafter.

The silicon substrate provided may be a thin monocrystalline or multicrystalline silicon wafer or else a silicon thin layer.

The surface to be coated may be the front of the solar cell substrate that faces the incident light during use. In this case, the second dielectric layer is applied preferably as an antireflection layer, i.e. at a thickness at which negative interferences occur for the incident and reflected light. The thickness may be selected in the range from about 50 to 150 nm, depending on the index of refraction of the material used for the second dielectric layer.

Alternatively, the surface to be coated may be the back of the solar cell substrate that is remote from the incident light during use. In this case, the second dielectric layer is embodied preferably as what is known as a back surface reflector, so that light, in particular infrared light, which penetrates the entire solar cell, is for the most part reflected at this back surface and thus passes through the solar cell substrate a further time.

Before the depositing of the first dielectric layer, the surface of the silicon substrate can be thoroughly cleaned, so that no contamination remains thereon that might disturb the subsequently deposited dielectric layer. In particular, the surface of the silicon substrate can be slightly etched away, for example in a solution which on the one hand contains an oxidizing agent and which on the other hand contains hydrofluoric acid (HF) which etches away the oxidized silicon oxide. A suitable cleaning method known in the production of solar cells is for example what is known as RCA cleaning.

According to one embodiment of the method according to the invention, for the atomic layer deposition of the first dielectric layer, the silicon substrate is firstly flushed with an aluminium-containing compound comprising at least one of

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the components Al(CH₃)₃, AlCl₃, Al(CH₃)₂Cl and (CH₃)₂(C₂H₅)N:AlH₃, so that an aluminium-containing layer is deposited on the surface of the silicon substrate. Subsequently, the aluminium-containing layer is oxidized to higher valency in an oxygen-containing atmosphere.

During the flushing of the silicon substrate with the aluminium-containing compound, the aluminium-containing compound can cling to the silicon surface at the points at which it enters into contact with the silicon surface. A chemical reaction with the silicon surface can occur; this is also referred to as chemisorption. In the best of cases, this can lead to the formation of a monomolecular layer made up of molecules of the aluminium-containing compound. It may be advantageous in this regard that this molecular layer can be almost perfectly tight, i.e. on correct selection of the processing parameters, such as duration and temperature during flushing, the entire silicon surface is covered with molecules of the aluminium-containing compound. This allows the subsequently produced first dielectric layer to be substantially atomically or molecularly tight.

In a subsequent processing step, the previously deposited molecular layer of the aluminium-containing compound is oxidized to higher valency. This can take place for example by flushing with oxygen or an oxygen-containing gas. In order to speed up the chemical reactions, the oxygen can be provided in the form of a high-energy O₂ plasma (plasma enhanced deposition), wherein it may be advantageous to ignite the O₂ plasma not directly above the substrates but in a separate chamber and then to guide it to the substrates (what is known as "remote plasma ALD"). Alternatively, the oxygen can be introduced at high temperatures (thermally enhanced deposition). A layer is then formed that at least contains Al₂O₃ molecules and that preferably consists entirely of Al₂O₃ molecules. It is in this way possible for a substantially monomolecular layer made up of Al₂O₃ molecules to be deposited at a thickness of about 1.2 angstroms (0.12 nm).

The process described hereinbefore can be repeated several times in order to achieve a sufficient thickness of the aluminium oxide layer. This draws on the fact that the molecules of the aluminium-containing compound cannot stick to one another, but can stick to the aluminium oxide molecules which are subsequently oxidized to higher valency. The first dielectric layer can thus be constructed layer by layer, allowing very good homogeneity and thus quality of the layer to be effected.

The entire sequential deposition process can be carried out in a common chamber into which the aluminium-containing compound is firstly introduced, that is subsequently flushed, and into which subsequently the oxygen-containing atmosphere is introduced before the process can then start up again.

An essential advantage of the atomic layer deposition is the fact that the entire substrate surface is coated uniformly. The deposition takes place irrespective of the geometry of the substrate surface, i.e. it is conform to the surface. The first dielectric layer is therefore deposited at the same thickness all over. This is beneficial in particular in surface-textured solar cells or in solar cells with channels which are intended to electrically contact the front with the back of the solar cell (what are known as EWT (emitter wrap through) solar cells), as passivation of the entire relevant solar cell surface can be ensured.

According to one embodiment of the method according to the invention, the second dielectric layer comprises silicon nitride, silicon oxide and/or silicon carbide. These materials display very good optical properties such as for example

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high transparency in almost the entire solar spectrum. They are therefore particularly suitable as the antireflection layer. Furthermore, dielectric layers made of these materials can contain a high hydrogen content; this can help to further passivate the solar cell.

According to one embodiment of the method according to the invention, the second dielectric layer is produced by means of a PECVD method. This method, in which reactants such as for example silane (SiH_4), dinitrogen oxide (N_2O), carbon dioxide (CO_2), ammonia (NH_3) and/or methane (CH_4) are reacted by igniting a plasma, can produce high-quality dielectric layers which are made of silicon nitride, silicon oxide or silicon carbide and can in addition have a high hydrogen content.

According to one embodiment of the method according to the invention, the second dielectric layer is deposited in such a way that it has a hydrogen content of at least 1 at. %, preferably at least 2 at. % and more preferably at least 5 at. %. The embedded hydrogen can diffuse at least in part through the first dielectric layer positioned therebelow and contribute to passivation there by saturating free bonds of the silicon ("dangling bonds"). It has been found that this contribution can even be still higher than in the case in which a hydrogen-containing dielectric is deposited directly on a silicon surface.

According to one embodiment of the method according to the invention, a high-temperature step is carried out at temperatures above 600°C ., preferably above 700°C . and more preferably above 800°C ., after the depositing of the second dielectric layer. A high-temperature step of this type can for example be used to fire, during further processing of the solar cell, metal contacts, which were printed beforehand onto the solar cell surface by means of screen printing, into the solar cell. The high-temperature step can in this case have the further advantage that hydrogen contained in the second dielectric layer can easily diffuse at the elevated temperatures through the first dielectric layer and saturate bonds of the silicon that are still free; this can lead to a further improvement in the passivating effect.

According to one embodiment of the method according to the invention, the first dielectric layer is deposited at a thickness of less than 50 nm, preferably less than 30 nm and more preferably less than 10 nm. Even at very low thicknesses, the first dielectric layer offers very good surface-passivating properties on account of its high quality which can be achieved as a result of the atomic layer deposition. The thinner the layer is, the more rapidly it can be deposited, although a minimum thickness of about 0.5 nm, preferably about 2 nm, should not be undershot in order to ensure tightness of the layer.

According to one embodiment of the method according to the invention, the second dielectric layer is deposited at a thickness of more than 50 nm, preferably more than 100 nm and more preferably more than 200 nm. As described hereinbefore, the thickness of the second dielectric layer can be adapted to its task as the antireflection layer or back surface reflector.

According to a second aspect of the present invention, a solar cell is proposed comprising a silicon substrate; a first dielectric layer comprising aluminium oxide on a surface of the silicon substrate; and a second dielectric layer on a surface of the first dielectric layer, the materials of the first and the second dielectric layer differing and hydrogen being embedded into the second dielectric layer.

It should be noted that the embodiments, features and advantages of the invention have been described mainly in relation to the manufacturing method according to the

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invention. However, a person skilled in the art will recognise both from the foregoing and from the subsequent description that, unless otherwise indicated, the embodiments and features of the invention are also transferable by analogy to the solar cell according to the invention. In particular, the features of the various embodiments may also be combined with one another in any desired manner.

In summary, the method or the solar cell according to aspects and embodiments of the present invention is distinguished from previously known methods for the surface passivation of crystalline silicon solar cells or solar cells coated in this way inter alia in terms of the following points:

- (i) very good surface passivation, such as is necessary for achieving high degrees of solar cell efficiency, can be achieved even after a firing step in the temperature range of $800\text{--}900^\circ\text{C}$;
- (ii) both low and high doped n- and p-type silicon surfaces can be passivated very effectively;
- (iii) on account of the high negative charge density in the Al_2O_3 layer on p-type silicon, no inversion layer is induced below the passivating layer in the silicon, allowing the harmful effect of a "parasitic shunt" to be substantially avoided;
- (iv) the layers contain no pinholes;
- (v) it is possible to achieve in a simple manner very good optical properties of the layer system that can be adapted very easily to the requirements of the solar cell by way of the thickness and the composition of the, for example PECVD-deposited, layer, so that the layer system can for example be embodied as an antireflection layer on the front of the solar cell or as an infrared reflector on the back of the solar cell in combination with a metal coating over the entire surface of the passivating layer.

BRIEF DESCRIPTION OF THE DRAWINGS

Further features and advantages of the present invention will become apparent to the person skilled in the art from the subsequent description of an exemplary embodiment, although this is not to be interpreted as restricting the invention, and with reference to the accompanying drawing, in which:

FIG. 1 illustrates schematically a solar cell according to one embodiment of the present invention.

DETAILED DESCRIPTION OF EMBODIMENTS

An exemplary embodiment of the manufacturing method according to the invention will be specified hereinafter.

A silicon wafer 1, which has not yet been fully processed to form the solar cell and into which an emitter on a surface was, for example, diffused beforehand and the surface of which was cleaned thoroughly, is introduced into an evacuated coating chamber and an Al-containing compound, such as for example $\text{Al}(\text{CH}_3)_3$, is fed into the chamber as a reactant. Chemisorption causes the molecules of the reactant to be deposited on the silicon surface until the surface is saturated. The non-chemisorbed molecules of the reactant are subsequently removed from the chamber, for example in that the chamber is flushed with a flushing gas such as for example nitrogen.

Subsequently, an O_2 plasma is ignited above the silicon surface to be passivated or in a separate chamber and the oxygen radicals react with the chemisorbed molecules to form Al_2O_3 . In the best of cases, a monomolecular aluminium oxide layer is formed. The temperature of the silicon

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wafer is in this case kept as constantly as possible at a temperature which is in the range between room temperature and 450° C.

After a cycle of this type, the coating chamber is evacuated again and a new cycle commences. This process is repeated until the desired thickness of the Al₂O₃ layer is reached. In order to keep the total coating duration as short as possible, the layer thickness of the Al₂O₃ layer 3 is limited to about 5 nm, i.e. the ALD coating process is repeated about 40 to 50 times, resulting in a total coating duration of from about 20 to 200 s.

The variant of ALD described herein is referred to as "plasma-assisted ALD" and is well known from the literature; see for example C. W. Jeong et al., Plasma-assisted atomic layer growth of high-quality aluminum oxide thin films, *Jpn. J. Appl. Phys.* 40, 285-289 (2001). Tests have shown that particularly good surface passivation can be achieved in that the plasma does not have direct contact to the substrates, as, in the event of such contact, ion bombardment can damage the substrate surfaces, but rather burns in a separate chamber from which the radicals are subsequently guided to the substrate surface. This variant of the method is referred to as "remote plasma-assisted ALD" and is described in U.S. Pat. No. 7,410,671, for example.

Alternatively, the Al₂O₃ thin layer 3 can also be deposited by means of thermal ALD, as described in the literature in M. Ritala et al., Atomic layer deposition of oxide thin films with metal alkoxides as oxygen sources, *Science* 288, 319-321 (2000), for example.

The Al₂O₃ thin layer 3 deposited on the silicon wafer is subsequently coated in a PECVD reactor with a silicon oxide thin layer 5 in a continuous process at a high deposition rate. The deposition temperature is in this case in the range between room temperature and 450° C. The gases used are SiH₄ and N₂O.

N₂O can in this case also be replaced by CO₂. It is also possible to deposit a silicon nitride layer by exchanging the N₂O for NH₃ or to deposit a silicon carbide layer by exchanging the N₂O for CH₄. If the deposition takes place at temperatures below 400° C., subsequent tempering for approx. 30 min in the temperature range of 400-500° C. can have a positive effect in order to achieve the optimum passivating quality of the layer system.

Finally, metal contacts 7, 9 are applied, for example by means of screen printing, to the front and the back of the coated silicon substrate and fired-in in a continuous furnace at about 700-900° C.

In summary and in other words, aspects of the present invention may be described as follows:

A method is proposed for forming a stack layer, the stack layer consisting of two partial layers:

(i) a very thin (for example 10 nm) aluminium oxide thin layer formed by atomic layer deposition (ALD) from an aluminium-containing gas (for example trimethylaluminium Al(CH₃)₃), and also
(ii) a thicker (>30 nm) silicon oxide-containing thin layer which can be formed, for example by means of plasma enhanced chemical vapour deposition (PECVD), from the gases silane (SiH₄) and dinitrogen oxide (N₂O) or carbon dioxide (CO₂).

The second layer may also be, instead of a silicon oxide thin layer, a silicon nitride-containing thin layer formed from the gases silane (SiH₄) and ammonia (NH₃) by means of PECVD, or a silicon carbide-containing thin layer formed from the gases silane (SiH₄) and methane (CH₄). The thin layers made of silicon oxide, silicon nitride or silicon carbide, which are deposited by means of PECVD, have a

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very high hydrogen content (for example >5 at. %) and therefore serve as a source of hydrogen during a firing step in the temperature range of 700-900° C. The hydrogen diffuses through the ultrathin Al₂O₃ layer and passivates unsaturated silicon bonds ("dangling bonds") at the Si/Al₂O₃ interface, leading to very good surface passivation after the firing step. In this way, the combination according to the invention of the two known deposition methods, ALD and PECVD, allows the formation of a firing-stable passivating layer which is optimally suitable for solar cells.

The invention claimed is:

1. Method for manufacturing a silicon solar cell, including the following steps:

providing a silicon substrate;

depositing a first dielectric layer having a thickness of less than 50 nm on a surface of the silicon substrate by means of atomic layer deposition, wherein the first dielectric layer comprises aluminium oxide; and

depositing a second dielectric layer directly on a surface of the first dielectric layer, materials of the first dielectric layer and the second dielectric layer differing and hydrogen being embedded into the second dielectric layer.

2. The method according to claim 1, wherein, for the depositing the first dielectric layer, the silicon substrate is firstly flushed with an aluminium-containing compound comprising at least one of Al(CH₃)₃, AlCl₃, Al(CH₃)₂Cl and (CH₃)₂(C₂H₅)N:AlH₃, so that an aluminium-containing layer is deposited on the surface of the silicon substrate, and wherein the aluminium-containing layer is subsequently oxidized to higher valency in an oxygen-containing atmosphere.

3. The method according to claim 1, wherein the second dielectric layer comprises a material selected from the group consisting of silicon nitride, silicon oxide and silicon carbide.

4. The method according to claim 1, wherein the second dielectric layer is manufactured by means of a PECVD method.

5. The method according to claim 1, wherein the second dielectric layer is deposited in such a way that the second dielectric layer has a hydrogen content of at least 1 at. %.

6. The method according to claim 1, wherein a high-temperature step is carried out at temperatures above 600° C. after the depositing of the second dielectric layer.

7. The method according to claim 1, wherein no further dielectric layers are deposited on the surface of the silicon substrate on which the first dielectric layer and the second dielectric layer are deposited.

8. The method according to claim 1, wherein the first dielectric layer is deposited with a thickness of less than 30 nm.

9. The method according to claim 1, wherein, for the depositing the first dielectric layer, the silicon substrate is firstly flushed with an aluminium-containing compound comprising at least one of Al(CH₃)₃, AlCl₃, Al(CH₃)₂Cl and (CH₃)₂(C₂H₅)N:AlH₃, so that an aluminium-containing layer is deposited on the surface of the silicon substrate, and wherein the aluminium-containing layer is subsequently oxidized to higher valency in an oxygen-containing atmosphere; and

wherein a high-temperature step is carried out at temperatures above 600° C. after the depositing of the second dielectric layer.

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10. The method according to claim 1, wherein the second dielectric layer comprises a material selected from the group consisting of silicon nitride, silicon oxide and silicon carbide;

wherein the second dielectric layer is manufactured by means of a PECVD method;
wherein the second dielectric layer is deposited in such a way that the second dielectric layer has a hydrogen content of at least 1 at. %; and
wherein the second dielectric layer is deposited at a thickness of more than 50 nm.

11. The method according to claim 1, wherein, for the depositing the first dielectric layer, the silicon substrate is firstly flushed with an aluminium-containing compound comprising at least one of $Al(CH_3)_3$, $AlCl_3$, $Al(CH_3)_2Cl$ and $(CH_3)_2(C_2H_5)N:AlH_3$, so that an aluminium-containing layer is deposited on the surface of the silicon substrate, and wherein the aluminium-containing layer is subsequently oxidized to higher valency in an oxygen-containing atmosphere;

wherein the second dielectric layer comprises a material selected from the group comprising of silicon nitride, silicon oxide and silicon carbide;
wherein the second dielectric layer is manufactured by means of a PECVD method;
wherein the second dielectric layer is deposited in such a way that the second dielectric layer has a hydrogen content of at least 1 at. %;
wherein a high-temperature step is carried out at temperatures above 600° C. after the depositing of the second dielectric layer; and
wherein the second dielectric layer is deposited at a thickness of more than 50 nm.

12. A solar cell comprising:
a silicon substrate;

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a first dielectric layer comprising aluminium oxide on a surface of the silicon substrate; and
a second dielectric layer directly on a surface of the first dielectric layer, materials of the first dielectric layer and the second dielectric layer differing and hydrogen being embedded into the second dielectric layer;
wherein the first dielectric layer has a thickness of less than 50 nm and is interposed between the surface of the silicon substrate and the second dielectric layer.

13. The solar cell according to claim 12, wherein the second dielectric layer comprises a material selected from the group consisting of silicon nitride, silicon oxide and silicon carbide.

14. The solar cell according to claim 12, wherein the first dielectric layer has a thickness of less than 30 nm.

15. The solar cell according to claim 12, wherein the first dielectric layer is deposited by means of atomic layer deposition, so that the first dielectric layer is substantially atomically tight;

wherein the second dielectric layer comprises a material selected from the group consisting of silicon nitride, silicon oxide and silicon carbide;
wherein the second dielectric layer has a thickness of more than 50 nm; and
wherein the first dielectric layer has a thickness of less than 50 nm.

16. A solar cell comprising:
a silicon substrate; and
a dielectric double layer consisting of
a first dielectric layer comprising aluminum oxide on a surface of the silicon substrate, and
a second dielectric layer directly on a surface of the first dielectric layer, materials of the first dielectric layer and second dielectric layer differing and hydrogen being embedded in the second dielectric layer.

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CIVIL COVER SHEET

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I. (a) PLAINTIFFS

HANWHA Q CELLS & ADVANCED MATERIALS CORPORATION

(b) County of Residence of First Listed Plaintiff Korea (EXCEPT IN U.S. PLAINTIFF CASES)

(c) Attorneys (Firm Name, Address, and Telephone Number) Adam W. Poff, Young Conaway Stargatt & Taylor, LLP, 1000 North King Street, Wilmington, DE 19801, (302) 571-6600

DEFENDANTS

REC SOLAR HOLDINGS AS, REC SOLAR PTE. LTD., and REC AMERICAS, LLC

County of Residence of First Listed Defendant (IN U.S. PLAINTIFF CASES ONLY)

NOTE: IN LAND CONDEMNATION CASES, USE THE LOCATION OF THE TRACT OF LAND INVOLVED.

Attorneys (If Known)

II. BASIS OF JURISDICTION (Place an "X" in One Box Only)

- 1 U.S. Government Plaintiff, 2 U.S. Government Defendant, 3 Federal Question (U.S. Government Not a Party), 4 Diversity (Indicate Citizenship of Parties in Item III)

III. CITIZENSHIP OF PRINCIPAL PARTIES (Place an "X" in One Box for Plaintiff and One Box for Defendant)

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VIII. RELATED CASE(S) IF ANY

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DATE 03/05/2019 SIGNATURE OF ATTORNEY OF RECORD /s/ Adam W. Poff

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RECEIPT # AMOUNT APPLYING IFP JUDGE MAG. JUDGE

The following related actions are being filed by Hanwha Q CELLS & Advanced Materials Corporation today in the United States District Court for the District of Delaware:

1. Hanwha Q CELLS & Advanced Material Corporation v. JinkoSolar Holding Co., Ltd., *et al.*, C.A. No. _____;
2. Hanwha Q CELLS & Advanced Material Corporation v. LONGi Green Energy Technology Co., Ltd., *et al.*, C.A. No. _____.