Method for passivating at least a part of a substrate surface

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(71) Applicant *(for all designated States except US)*: **OTB SOLAR B.V.** [NL/NL]; Luchthavenweg 10, NL-5657 EB Eindhoven (NL).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **ILLIBERI, Andrea** [IT/NL]; Sint Martinusstraat 2B, NL-5615 PK Eindhoven (NL). **HOEX, Bram** [NL/SG]; Parc Oasis, 51 Jurong East Avenue 1, # 13-03, Singapore 609782 (SG). **KESSELS, Wilhelmus Mathijs Marie** [NL/NL]; Bijsterveldenlaan 12, NL-5045 ZZ Tilburg (NL). **VAN DE SANDEN, Mauritius Cornelis Maria** [NL/NL]; P.F. Bergmansstraat 4, NL-5017 JH Tilburg (NL).

(74) Agent: **Hatzmann, M., J.**; Vereenigde, Johan de Wittlaan 7, NL-2517 JR Den Haag (NL).

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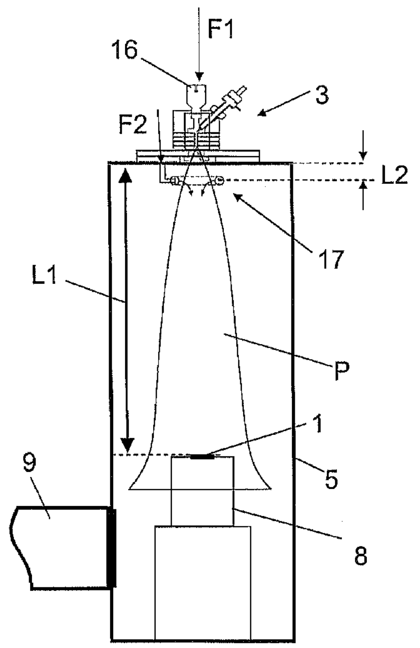

FIG.1

(57) Abstract: A method for passivating at least a part of a surface of a semiconductor substrate, wherein at least one layer comprising at least one a-Si:H passivation layer is realized on said part of the substrate surface by: - generating a plasma (P) by means of at least one plasma source (3) mounted on the process chamber (5) at a distance (L) from the substrate surface, at least part of the plasma (P) being injected into the chamber (5) and achieving a supersonic speed; - contacting at least a part of the plasma (P), injected into the chamber (5), with the said part of the substrate surface; and - supplying at least one precursor suitable for passivation layer realization to the said part of the plasma (P) via a plurality of injection nozzles (19) of an injector device (17), such that the density of the precursor at each injection nozzle (19) is lower than $12x10^{22}$ particles/m^3.

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Title: Method for passivating at least a part of a substrate surface

The present invention relates to a method for passivating at least a part of a surface of a semiconductor substrate, wherein at least one layer comprising at least one passivation layer is realized on said part of the substrate.

Passivation of the substrate surface is desired for various applications, for example in the field of solar cell manufacturing. The extent of surface passivation is usually expressed by the surface recombination velocity (SRV). A good surface passivation of the semiconductor substrate usually means a relatively low surface recombination velocity (i.e. long effective lifetimes of the electrons/holes in the material).

In known methods, a substrate surface of a semiconductor substrate is passivated by realizing a SiO_x layer, for instance a layer of silicon oxide, on that surface. Here, for instance, use can be made of an oxidation method in an oven. However, known oxidation methods require elaborate processing and long oxidation times.

Also, in a known method, a SiN_x:H layer is deposited on the surface of the substrate, to passivate the surface, see the publication “High rate deposition of a-SiN_x:H for photovoltaic applications by the expanding thermal plasma” of Kessels et al., J. Vac. Sci. Technol. A 20(5), Sep/Oct 2002.

Recently, hydrogenated amorphous silicon (a-Si:H) has been named a suitable alternative, for passivating substrate surfaces. A recent paper titled “State-of-the- art surface passivation by hydrogenated amorphous silicon deposited at rates > 1 nm/s by the espanding plasma technique” (B. Hoex, W.M.M. Kessels, M.D. Bijker, and M.C.M. van de Sanden, Proceedings of the 21th European PVSEC, Dresden, 435, 2006). describes application of the expanding thermal plasma (ETP) technique to deposit the a-Si:H layer. The films were deposited using a reactor having an ETP source, generating an argon-hydrogen (Ar-H_2) plasma which expends supersonically through a nozzle into a deposition chamber (kept at a pressure of 0.2 mbar) towards the substrate. Monosilane (SiH_4) was injected in the plasma expansion via an injection ring located 5 cm from the plasma source. The paper shows that a-Si:H with an excellent level of surface passivation was deposited at a substrate temperature of 400 ^{0}C. A pre-anneal effective surface recombination velocity of 15 cm/s was obtained (using a c-Si substrate) that was passivated on both sides with a 80 nm thick a-Si:H film. Figure 6 of the paper indicates an effective lifetime of 1 to 2 msec. However, according to the paper, a single side deposited yielded effective surface recombination velocities in the order of 6 cm/s, indicating thermal degradation of the a-Si:H film. Also, according to the paper even though the a-Si:H was deposited at 400 ^{0}C, it was not thermally stable. According to the paper, prolonged high temperatures should be avoided during lifetime testing and in the process flow of an industrial process when using a-Si:H as a surface passivation layer.

The present invention contemplates obviating above-mentioned drawbacks of known methods. In particular, the invention contemplates to improve the a-Si:H based passivation method, aiming at providing a stable surface passivation, and achieving low surface recombination velocities and long effective electron/hole lifetimes.

To this end, the method according to the invention is characterized in that at least one layer comprising at least one a-Si:H passivation layer is realized on at least part of the substrate surface by:

- placing the substrate in a process chamber;

- maintaining the pressure in the process chamber at a vacuum pressure;

- maintaining the substrate at a substrate treatment temperature suitable for realizing said layer;

- generating a plasma by means of at least one plasma source mounted on the process chamber at a distance from the substrate surface, at least part of the plasma being injected into the chamber and achieving a supersonic speed;

- contacting at least a part of the plasma, injected into the chamber , with the said part of the substrate surface; and

- supplying at least one precursor suitable for the a-Si:H passivation layer realization to the said part of the plasma via a plurality of injection nozzles of an injector device, such that the density of the precursor at each injection nozzle is lower than $12x10^{22}$ particles/m^3.

Surprisingly, it has been found more stable passivation are obtained (providing relatively little degradation in the effective lifetime compared to previous methods) in case the precursor is injected into the chamber at a relatively low density (i.e., the low density being measured in the injection nozzle). The best experimental result achieved with the present method is a relatively thick a-Si:H surface passivation layer (thickness 85 nm) providing an initial lifetime of 8.0 ms. The lifetime decreased to 5.3 ms after 16 days (i.e. a loss of only 34%). A thin surface passivation layer (6 nm), manufactured by the method, also provided a good passivation lifetime of 1.1. ms.

According to a preferred embodiment, the precursor is injected into the plasma from more than eight separate injection openings, for example more than fifteen openings; thus, relatively high precursor supply rates can be utilized, the large number of injection openings providing desired relatively low precursor densities (in those openings) prior to injection. For example, according to a preferred embodiment, the overall flow rate of the precursor (fed to the plurality of injection nozzles/openings) is higher than 1 sccs (standard cubic centimeters per second), for example about 10 sccs or more than 10 sccs. A flow rate of precursor through each injector nozzle can be, for example, lower than 1.25 sccs.

Also, a second aspect of the invention is characterized by the features of claim 29, which can be combined with the above-mentioned method according to the invention. According to the second aspect of the invention, the pressure in the process chamber is lower than 0.1 mbar. It has been found that application of this low pressure can also lead to an improved passivation layer, providing relatively long effective electron/hole lifetimes.

A third aspect of the invention is characterized by the features of claim 30, which can be combined with the above-mentioned method according to the invention, with the second aspect of the invention, or both. According to the third aspect of the invention, the precursor is injected into the chamber via a number of injection nozzles, a lateral distance between a centre line of the plasma and each injection nozzle being larger than 4 cm. For example, the injector can be an injector ring, having a internal diameter of more than 8 cm (for example a diameter of about 10 cm or larger). It has been found that application of a relatively large distance between a precursor injection point and the plasma centre line can lead to improved passivation layers as well.

Furthermore, the invention provides an apparatus for realizing at least one layer onto at least part of a surface of a substrate, the apparatus comprising:

- a process chamber, having a substrate holder for holding a substrate;

- at least one remote plasma source mounted on the process chamber at a distance from the substrate holder, for generating a plasma that expands into the chamber;

-an injector device for supplying at least one precursor suitable for layer realization to the expanding plasma.

Good results have been obtained by application of an injector device that is provided with more than eight separate precursor injection nozzles, and preferably more than fifteen. Also, good results have been obtained by application of an injector device provided with a number of nozzles, a total, cumulative, injection surface defined by the number of injection nozzles being larger than 7 mm^2, particularly larger than 10 mm^2. It is thought that the improved injector device can lead to better dissociation of the precursor, after being injected into the plasma. Also, the improved injector device can achieve relatively low precursor injection during operation, at predetermined overall precursor supply rates.

Also, the invention provides a solar cell, provided with at least a part of a substrate at least obtained with a method according to any one of the claims 1-30.

Further advantageous embodiments of the invention are described in the dependent claims. These and other aspects of the invention will be apparent from and elucidated with reference to non-limiting embodiments described hereafter, shown in the drawings.

Fig. 1 schematically shows a schematic cross-sectional view of a substrate treatment apparatus;

Fig. 2 shows part of the apparatus in more detail;

Fig. 3 shows part of an example of an injector device of the apparatus show in Fig 1; and

Fig. 4 depicts a detail of a radially inner surface of the injector device.

In this patent application, same or corresponding measures are designated by same or corresponding reference symbols. In the present application, a value provided with a term like "approximately", "substantially", "about" or a similar term can be understood as being in a range between that value minus 5% of that value on the one hand and that value plus 5% of that value on the other hand.

Figures 1-2 show an apparatus with which at least a deposition or realization of at least one passivation layer, and for instance one or more other layers on a substrate can be carried out, in a method according to the invention. The apparatus is, for instance, well suitable for use in an inline process. The apparatus is provided with a process chamber 5 on which a DC (direct current) plasma cascade source 3 is provided. Alternatively, a different type of plasma source may be used. The DC plasma cascade source 3 of the exemplary embodiment is arranged for generating a plasma with DC voltage. The apparatus is provided with a substrate holder 8 for holding one substrate 1 opposite an outflow opening 4 of the plasma source 3 in the process chamber 5. The apparatus further comprises heating means (not shown) for heating the substrate 1 during layer realization.

The plasma cascade source 3 is provided with one or more cathodes 10 (one being shown) located in a front chamber 11 and an anode 12 located at a side of the source 3 proximal to the process chamber 5. The front chamber 11 opens into the process chamber 5 via a relatively narrow channel 13 and the above-mentioned plasma outflow opening 4. The apparatus is, for instance, dimensioned such that the distance L1 between the substrate 1 and the plasma outflow opening 4 is approximately 30 mm – 70 cm, more particularly 40-60 cm, for example about 55 cm. The channel 13 can be bounded by mutually electrically insulated cascade plates 14 and the above-mentioned anode 12.

During treatment of a substrate 1, the process chamber 5 is kept at a relatively low pressure, particularly lower than 5000 Pa, and preferably lower than 500 Pa. Of course, *inter alia* the treatment pressure and the dimensions of the process chamber need to be such that the growth process can still take place. In practice, according to an aspect of the present invention, good passivation results are obtained in case the treatment pressure smaller than 0.2 mbar, for example in the range of about 0.05-0.1 mbar, and preferably smaller than 0.1 mbar. An exhaust of a pumping system, to obtain the above-mentioned treatment pressure, is indicated at reference sign 9 in the drawing.

Between each cathode 10 and anode 12 of the source 3, a plasma is generated during use, for instance by ignition of an inert gas, such as argon, which is present therebetween. When the plasma has been generated in the source 3, the pressure in the front chamber 11 is higher than the pressure in the process chamber 5. This pressure can, for instance, be substantially atmospheric and be in the range of 0.5-1.5 bar. It has been found that good results can be achieved in case the pressure in the source front chamber 11 is sub-atmospheric, for example in the range of 0.1-0.5 bar, particularly 0.1-0.2 bar. Because the pressure in the process chamber 5 is considerably lower than the pressure in the front chamber 6, a part of the generated plasma P expands such that it extends via the relatively narrow channel 7 from the above-mentioned outflow opening 4 into the process chamber 5 for contacting the surface of the substrate 1. In the present invention, the expanding plasma part reaches a supersonic velocity. Also, the expanding plasma P can have a rotational symmetrical configuration, particularly with respect to a centre line CL (which, in this example, extends centrally from the plasma outflow opening 4, and towards the substrate holder 8).

Since the plasma cascade source operates with DC voltage for generating the plasma, the passivation layer can simply be grown at a constant growth rate, substantially without adjustment during layer realization. This is advantageous compared to use of a plasma source driven with AC. Further, with a DC plasma cascade source, a relatively high growth rate can be obtained. It is found that, with this apparatus, a particularly good surface-passivated substrate can be obtained, in particular with a passivation layer, as will be explained below.

The apparatus is particularly provided with a fluid supply system 16, 71. Such supply system may be designed in different manners, which will be clear to a skilled person. In the exemplary embodiment, the supply system comprises, for instance, a plasma fluid supply 16 designed for introducing one or more fluids into the plasma source 3. Arrow F1 (in Fig. 1) indicates supply of the fluid to the source 3. In the present examples, during operating and in case of deposition of an a-Si:H passivation layer, a mixture of hydrogen (H_2) and the afore-mentioned inert gas (for example Argon) are fed via this supply 16 into the source, to generate a hydrogen containing plasma P.

The supply system further comprises, for instance, at least one injector device 17 for supplying one or more passivation layer precursor fluids to the plasma P downstream of the above-mentioned plasma outflow opening 4 (in this case below the plasma source 3, in the process chamber 5). Arrow F2 indicates supply of such precursor fluid to the injector device 17.

According to a further embodiment, the precursor that is injected via the device 17 into the apparatus can be a silane, for example monosilane SiH_4 or disilane Si_2H_6 (i.e., the precursor by itself can be an a-Si layer precursor). Such a precursor is suitable to realize an a-Si:H layer.

The treatment apparatus is provided with sources (not shown) which are connected to the above-mentioned supply system 16, 17 via flow control means, for supplying specific desired treatment fluids (i.e. layer realization precursors) thereto.

Particularly, the injector device 17 can be ring shaped, having a ring shaped inner wall (a section of which is shown in Fig. 4) surrounding a central aperture 18 (having a circular cross-section). The plasma P passes through the aperture 18 during operation. Preferably, the injector device is arranged concentrically with respect to the plasma P (see Fig. 1, 2).

The injector device 17 has a plurality of separate precursor injection nozzles 19 (i.e. outflow openings), one being shown in Fig. 4, for injecting the precursor fluid into the process chamber 5, and into the plasma P that passes the injector aperture 18. In the example, each nozzle 19 is a circular outflow opening (having diameter D2, for example a diameter D2 in the range of about 0.5-2 mm, for example about 1 mm). The device 17 includes one or more channels (not shown) for feeding the injector fluid (received from the upstream fluid supply, F2) to the nozzles 19. In the example, the nozzles are directed inwardly, for example towards a central point of the aperture 18. In this particular example, the device 17 has 16 separate nozzles 19. Precursor fluid flows, injected from the nozzles, are indicated by arrows S in the drawings. Thus, during operation, the precursor is injected into the plasma P from more than 8 separate injection openings 19, and particularly more than 15 openings 19.

Preferably, as in the example, the nozzles (i.e. outflow openings) 19 are arranged symmetrically, at equally spaced intervals with respect to the plasma P, with respect to a plasma centre line CL (see Fig. 2, 3). Moreover, each of the precursor outflow openings 19 is located at a certain a lateral distance R from the centre line CL of the plasma P (the lateral distance R in this case being half the inner diameter D1 of the ring shaped injector wall that is provided with the openings 19). Also, in the example, the injector device 17 is located downstream with respect to the plasma outflow opening 4, particularly at a distance L2 there-from (the distance L2 being measured from a transversal plane that centrally intersects each of the outflow openings 19, in a direction parallel with respect to the plasma centre line CL). In this embodiment, the downstream ring-shaped part of the injector is connected to the process chamber wall via one or more connector elements (17a) –one being shown-, which also include one or more ducts to feed the injector fluid towards the outflow openings/nozzles 19.

It has been found that application of a relatively large number of injector nozzles 19 leads to a significant improvement in passivation results. The injector 17 can achieve a more uniform injection of precursor material into the supersonically expanding plasma P. Particularly, without wishing to be bound to any theory, it is believed that this configuration can provide a relatively low density and pressure of the precursor (just after injection into the plasma P), at the same overall precursor flow rate (i.e. of the precursor flow F2, being supplied to the apparatus), leading to a higher precursor dissociation degree and improved passivation layer that is associated therewith.

Each injector nozzle 19 provides a certain injection surface area. Particularly in combination with application of a large number of separate nozzles 19, it has been found that good passivation results can be achieved in case a total, cumulative, injection surface defined by all the injection nozzles being larger than 7 mm^2, for example larger than 10 mm^2. In a further elaboration, in case sixteen nozzles 19 are present, each having a diameter D2 of 1 mm, the cumulative, injection surface is larger than 12 mm^2.

Also, application of an injector having a relatively large central aperture diameter D1 has led to improved passivation results. Particularly, the diameter D1 of the aperture 18 is larger than 8 cm, for example about 10 cm. Thus, also, in a further elaboration, the distance R between each precursor outflow opening 19 and the centre line CL of the plasma P (being half the diameter D1) is larger than 4 cm, for example about 5 cm.

Concerning the arrangement of the system, preferably, the longitudinal distance L2, measured in parallel with the centre line of the plasma, between each nozzle and the plasma source 3 can be in the range of 2-10 cm, more particularly 4-6 cm, for example about 5 cm

For the purpose of passivating the substrate 1, during use, the cascade source 3 generates a plasma P (for example an argon plasma P, optionally an argon-hydrogen plasma) in the described manner, such that the plasma P reaches supersonic speeds in the chamber 5, and contacts the substrate surface of the substrate 1. The afore-mentioned precursor (for example a silane) is supplied via the injector 17 to the plasma P. The process parameters of the plasma treatment process, at least the above-mentioned process chamber pressure, the substrate temperature (T_s), the distance L1 between the plasma source 3 and the substrate 1, and the flow rates of plasma fluids and precursor fluid are selected such that the apparatus deposits or realizes the passivation layer on the substrate 1 at an advantageous growth rate which is, for instance, larger than approximately 1 nm/s (for example a growth rate in the range of 1 nm/s to 20 nm/s).

Preferably, but not necessarily, a low chamber pressure is used, for example a pressure lower than 0.1 mbar. Good results have been obtained by application of a chamber pressure of 0.09 mbar.

Also, preferably, the precursor is being injected via the nozzles 19 of the injector device 17, such that the density of the precursor at each injection nozzle (19) is lower than $12x10^{22}$ particles/m^3, for example lower than $10x10^{22}$ particles/m^3, for example about $6x10^{22}$ particles/m^3 or lower. Particularly, the density is the precursor density, measured in the nozzle (outflow opening) itself.

In a further embodiment, a total flow rate g1 of the precursor, being injected into the chamber via the injector device 17, is higher than 1 sccs, for example 10 sccs or higher.

For example, the flow rate of precursor through each nozzle 19 of the injector device can be higher than 0.0625 sccs, for example higher than 0.1 sccs. In a further embodiment, a precursor flow rate, flowing from each nozzle 19 into the chamber, is lower than 1.25 sccs, for example lower than 1 sccs. In yet a further embodiment, a precursor flow rate, flowing from each nozzle 19 into the chamber, is lower than 0.7 sccs. Good results have been obtained using a precursor flow rate at each nozzle 19 in the range of 0.6-0.7 sccs.

Similarly, for example in case of a-Si:H realization, the total flow rate of hydrogen g2 can be about the same as the flow rate of the precursor. For example, in a non-limiting embodiment, a ratio g1/g2 of total silane precursor flow rate g1 and total hydrogen flow rate g2 can be in the range of 1/2 to 2/1.

During operation, a total flow rate g3 of an inert gas (for example argon) that is fed to the plasma source, to be ignited, can be higher than the total precursor flow rate g1. In a non-limiting embodiment, a ratio g3/g1 of inert gas flow rate g3 and precursor flow rate g1 can be in the range of 1/1 to 5/1, for example 2/1 to 3/1.

The substrate treatment temperature T_s can be in the range of 150 ^{0}C-500 ^{0}C, for example the range of 175 ^{0}C-400 ^{0}C. Experimental results have provided evidence of best passivation results using a substrate treatment temperature T_s is in the range of 200 ^{0}C-300 ^{0}C, for example about 250 ^{0}C.

The thickness of the passivation layer realized on the substrate can be in the range of 1-1000 nm. In one further elaboration, the layer thickness of is in the range of 50-150 nm, for example 60-100 nm. Alternatively, the layer thickness can be in the range of 1-20 nm, for example 1-10 nm.

According to a further example, the method can include depositing at least one second layer after realizing said passivation layer, preferably successively by the same apparatus. The second layer can act to prevent hydrogen (present in the layer) from escaping, thereby enhancing the stability of the surface passivation. Also, a further layer can be an anti-reflection coating. In a non-limiting embodiment, the second layer is an SiN_x layer. The thickness of the SiN_x layer can be in the range of approximately 25 to 100 nm, and may, for instance, be approximately 80 nm.

Experimental results

In an experiment, the above-described apparatus and method were used to passivate silicon (crystalline) wafer substrates, by deposition of hydrogenated amorphous silicon layers on the substrates. Both n-type and p-type silicon substrates (about 280 micron thick, 1-5 Ohm cm, having the <100> lattice structure) were investigated. The wafers were cleaned using RCA1 plus RCA2 and HF (2%) for 2 minutes, prior to being loaded into the treatment apparatus. Each loaded wafer was held at a distance L1 of 55 cm from the source's plasma exit opening.

A ring shaped injector device 17 as shown in Figures 3-4, having sixteen outflow openings 19, each having a diameter D2 of 1 mm, was installed in the apparatus. The inner diameter D1 of the injector 17 was 10.4 cm. The device 17 was positioned such, that longitudinal separation L2 between the nozzles 19 and the source outflow opening was 5 cm.

During layer deposition, a relatively low front chamber pressure of 160 mbar was applied. The pressure in the treatment chamber 5 was maintained at 0.09 mbar. Substrate temperatures T_s of 175 ^{0}C, 250 ^{0}C and 350 ^{0}C were used. A hydrogen-argon plasma P was generated in the source 3, using 25 sccs Ar and 10 sccs H_2 flow rates. SiH_4 was fed to the injector device 17 at a rate of 10 sccs (thus, the SiH_4 flowrate per outflow opening 19 was 0.625 sccs). In each case, the density of the SiH_4 precursor in each injection nozzle 19 was $6x10^{22}$ particles/m^3 (i.e. monosilane molecules per m^3).

A first part of the experiment involved depositing relatively thin a:Si-H layers (layer thicknesses 4 nm, 6 nm, and 7 nm). As a second part of the experiment, thick passivating layers (80 nm, 85 nm and 95 nm) were grown.

Surprisingly, it has been found that a relatively high deposition rate larger than 1.0 nm/s was achieved at a substrate temperature of only 175 ^{0}C. The growth rate of an 94 nm thick layer was 1.4 nm/s (T_s=175 ^{0}C), and the growth rate of an 7 nm thick layer was 1.1 nm/s.

Growth rates of 1.1. nm/s were also observed concerning deposition of a thick (85 nm) and thin (6 nm) layer at T_s= 250^0, and concerning deposition of a thick layer (80 nm) at T_s= 350^0. The deposition rate of a thin (4 nm) layer at T_s= 350^0 was just below 1 nm/s.

Lifetimes were measured by a photoconductance decay method (Sinton WCT100) in a transient mode. The lifetime measurements have provided evidence that the resulting samples provide very good surface passivation. In this experiment, the best result obtained was an initial lifetime of 8 ms (at an injection level of 10^{15} cm^{-3}) relating to the 85 nm sample (n-type wafer) grown at T_s=250 ^{0}C. After 15 days, this sample still achieved a lifetime of 5.3 ms (i.e. a loss of only 34%), which is still much higher than previously reported a-Si:H passivation lifetime measurement results. A 85 nm layer on a p-type wafer, deposited at T_s=250 ^{0}C, provided passivation with an initial lifetime of 2.6 ms, which decreased to 2.1 after 12 days.

Table 1 shows the initial lifetime results concerning all n-type samples. It follows that good -even excellent- passivation was achieved by deposition of the thick a-Si:H layers; the thin passivation layers provide lower life-times.

Deposition temperature	175 °C	250°C	350 °C
Lifetime Thickness	0.04 ms 7nm	1.1ms 6 nm	0.23 ms 4 nm
Lifetime Thickness	2.0 ms 95 nm	8.0ms 85nm	4.3 ms 80 nm

Table 1; lifetime measurement results (n-type samples)

Moreover, experiments were carried out (on a n-type sample having the 95 nm thick passivation layer, deposited at T_s=250 ^{0}C) to investigate thermal stability of the surface passivation. After layer deposition, the sample achieved a low surface recombination velocity (SRV) at in injection level 10^{15} cm^{-3} of 4 cm/s. In a first stability experiment, the sample was subjected to a thermal treatment of heating the sample to 180 ^{0}C for 30 minutes. After this experiment, the SRV was only a little higher than before the heating, achieving about 6 cm/s. Next, the same sample was heated (in an anneal step) for 10 minutes to a temperature of 400 ^{0}C. After that high temperature treatment, an SRV of 5 cm/s was observed. Thus, a thermally very stable passivation has been achieved in this case.

The experiments provided evidence of a porous layer (possibly hydrogen rich) formation at the beginning of the a-Si growth (a-Si:H/c-Si interface). Without wishing to be bound to theory it is believed that while the growth proceeds, a dense layer forms which can act as a cap to prevent hydrogen out-diffusion from the a-Si/c-Si interface during annealing, thus providing the thermal stability at 400 ^{0}C.

Also, the inventors expect that the application of a large number of separate precursor injection nozzles results in a relatively low density and pressure of precursor gas in the injector ring. This can induce a higher dissociation degree of the precursor by the plasma arc P, thus increasing the layer deposition rate. It is believed that a higher deposition rate will contribute to the formation of a porous (hydrogen rich) interface which provides the desired surface passivation.

Concluding, it has been found that the present method and apparatus can achieve realization of relatively thick (about 80-90nm) passivation layers, providing excellent surface passivation of n-type silicon substrates (best observed lifetime being 8ms) and p-type substrates (best lifetime being 2.6 ms). Moreover, relatively thin (6nm) passivation layers provide good passivation (lifetime 1.1 ms) of n-type c-Si; such passivated substrates can be good candidates for HIT (Heterojunction with Intrinsic Thin layer) solar cell production. Finally, and importantly, high layer deposition rates have been achieved (over 1 nm/s).

From the above it follows that an initial passivation may not be stable over time still, it follows that the stable levels reached are higher than previously reported results. Also, importantly, presently achieved passivation was found to be stable for an anneal step at 400 C for 10 min, thereby overcoming temperature stability problems that have been reported in the prior art.

Thus, improved results have already been obtained for deposition of a-Si:H layers.

It goes without saying that various modifications are possible within the framework of the invention as it is set forth in the following claims.

Thus, substrates of various semiconductor materials can be used to be passivated by the method according to the invention.

In addition, the method may, for instance, be carried out using more than one plasma source mounted on a process chamber.

In case of a-Si:H layer deposition, hydrogen can be injected into the plasma source 3, for example in a mixture with an inert gas. Alternatively, hydrogen can be injected into the plasma downstream with respect of the plasma source 3, for example via a suitable injector device, and/or together with a silane (acting as a-Si precursor). Besides, in combination, part of the hydrogen can be supplied to the plasma via the source 3, and part of the hydrogen can be supplied to the expanding plasma P downstream with respect of the source.

Further, the substrate may, for instance, be loaded into the process chamber 5 from a vacuum environment, such as a load lock brought to a vacuum and mounted to the process chamber. In that case, the pressure in the process chamber 5 can maintain a desired low value during loading. In addition, the substrate may, for instance, be introduced into the process chamber 5 when that chamber 5 is at an atmospheric pressure, while the chamber 5 is then closed and pumped to the desired pressure by the pumping means.

In the above-described experiments, best results were found to relate to substrate temperatures of 250 ^{0}C (during realization of the passivation layer, at a growth rate of 1.1 nm/s) The inventors expect that good passivation layers can also be manufactured at much higher growth rate and higher temperature (using the same apparatus and method), for example a temperature higher than 350 ^{0}C (and a growth rate higher than 2 nm/s. It is expected that a high growth rate and a high substrate temperature can provide a similar layer morphology, and respective surface passivation, as the morphology achieved at a substrate temperature of 250 ^{0}C and 1.1 nm/s deposition rate. Also, the inventors expect that the higher temperature substrate temperature during layer realization may further improve the stability of the passivation (after anneal).

Further, for instance, one or more layers can be applied to the substrate, for instance one or more a-Si:H layers and one or more optional other layers, for example one or more a-Si layers and/or one or more SiN_x layers.

Further, preferably, a whole surface of a substrate is passivated by means of a method according to the invention. Alternatively, for instance, only a part of the surface may be passivated by means of the method.

Further, the thickness of the a-Si:H layer realized on the substrate by means of the plasma treatment process may, for instance, be in the range of 1 nm - 1000 nm.

CLAIMS

1. A method for passivating at least a part of a surface of a semiconductor substrate, wherein at least one layer comprising at least one a-Si:H passivation layer is realized on said part of the substrate surface by:
- placing the substrate (1) in a process chamber (5);
- maintaining the pressure in the process chamber (5) at a vacuum pressure;
- maintaining the substrate (1) at a substrate treatment temperature suitable for realizing said layer;
- generating a plasma (P) by means of at least one plasma source (3) mounted on the process chamber (5) at a distance (L) from the substrate surface, at least part of the plasma (P) being injected into the chamber (5) and achieving a supersonic speed;
- contacting at least a part of the plasma (P), injected into the chamber (5), with the said part of the substrate surface; and
- supplying at least one precursor suitable for the a-Si:H passivation layer realization to the said part of the plasma (P) via a plurality of injection nozzles (19) of an injector device (17), such that the density of the precursor at each injection nozzle (19) is lower than $12x10^{22}$ particles/m^3.

2. A method according to claim 1 wherein the density of the a-Si:H layer precursor is at each injection nozzle (19) is lower than $1x10^{23}$ particles/m^3, for example about $6x10^{22}$ particles/m^3 or lower.

3. A method according to any of the preceding claims, wherein a total flow rate of the precursor, being injected, is higher than 1 sccs, for example 10 sccs or higher.

4. A method according to any of the preceding claims, wherein a flow rate of the precursor through each nozzle (19) is lower than 1.25 sccs, for example lower than 0.7 sccs.

5. A method according to any one of the preceding claims, wherein the precursor is a silane

6. A method according to claim 5, wherein the precursor is monosilane (SiH_4)

7. A method according to claim 5, wherein the precursor is an SiN_x:H layer.

8. A method according to any of the preceding claims, wherein a lateral distance (R) between a centre line of the plasma and each injection nozzle (19) is larger than 4 cm.

9. A method according to any of the preceding claims, wherein a longitudinal distance (L2), measured in parallel with the centre line of the plasma, between each nozzle (19) and the plasma source (3) is in the range of 2-10 cm, more particularly 4-6 cm.

10. A method according to any of the preceding claims, wherein the injector device (17) is ring shaped.

11. A method according to any of any of the preceding claims, wherein the injector device (17) is provided with an aperture (18), the plasma passing through the aperture, a diameter of the aperture being larger than 8 cm, for example about 10 cm or larger.

12. A method according to any of the preceding claims, wherein a total, cumulative, injection surface defined by the number of injection nozzles is larger than 7 mm^2.

13. A method according to any of the preceding claims, wherein a total, cumulative, injection surface defined by the number of injection nozzles is larger than 12 mm^2.

14. A method according preceding claims, wherein the precursor is injected into the plasma from more than 8 separate injection openings (19), for example more than 15 openings (19).

15. A method according to claim 14, wherein the openings (19) are arranged symmetrically, at equally spaced intervals with respect to the plasma, with respect to a plasma centre line.

16. A method according to any of the preceding claims, wherein the pressure in the process chamber is lower than 0.2 mbar.

17. A method according to any of the preceding claims, wherein the pressure in the process chamber is lower than 0.1 mbar.

18. A method according to any of the preceding claims, wherein the pressure in the process chamber is in the range of 0.05-0.1 mbar.

19. A method according to any of the preceding claims, wherein the substrate treatment temperature is in the range of 150 ^{0}C-500 ^{0}C, for example the range of 175 ^{0}C-400 ^{0}C.

20. A method according to any of the preceding claims, wherein the substrate treatment temperature is in the range of 200 ^{0}C-300 ^{0}C

21. A method according to any of the preceding claims, wherein a growth rate of the passivation layer is larger than 1 nm/s.

22. A method according to any one of the preceding claims, wherein hydrogen is supplied to the plasma via the plasma source.

23. A method according to any of the preceding claims, wherein the plasma is an argon plasma.

24. A method according to any one of the preceding claims, wherein the thickness of the passivation layer realized on the substrate (1) by means of the plasma treatment process is in the range of 1-1000 nm.

25. A method according to any one of the preceding claims, wherein the thickness of the passivation layer realized on the substrate (1) by means of the plasma treatment process is in the range of 50-150 nm, for example 60-100 nm.

26. A method according to any one of the claims 1-24, wherein the thickness of the passivation layer realized on the substrate (1) by means of

the plasma treatment process is in the range of 1-20 nm, for example 1-10 nm.

27. A method according to any one of the preceding claims, wherein the at least one plasma source comprises at least one plasma cascade source (3).

28. A method according to any one of the preceding claims, including depositing at least one second layer after realizing said passivation layer, preferably successively by the same apparatus.

29. A method for passivating at least a part of a surface of a semiconductor substrate, wherein at least one layer comprising at least one a-Si:H passivation layer is realized on said part of the substrate surface by:

- placing the substrate (1) in a process chamber (5);
- maintaining the pressure in the process chamber (5) at a vacuum pressure;
- maintaining the substrate (1) at a substrate treatment temperature suitable for realizing said layer;
- generating a plasma (P) by means of at least one plasma source (3) mounted on the process chamber (5) at a distance (L) from the substrate surface, at least part of the plasma (P) being injected into the chamber (5) and achieving a supersonic speed;
- contacting at least a part of the plasma (P), injected into the chamber (5), with the said part of the substrate surface; and
- supplying at least one precursor suitable for a-Si:H passivation layer realization to the said part of the plasma (P);

wherein the pressure in the process chamber is lower than 0.1 mbar.

30. A method for passivating at least a part of a surface of a semiconductor substrate, wherein at least one layer comprising at least one a-Si:H passivation layer is realized on said part of the substrate surface by:

- placing the substrate (1) in a process chamber (5);
- maintaining the pressure in the process chamber (5) at a vacuum pressure;
- maintaining the substrate (1) at a substrate treatment temperature suitable for realizing said layer;

- generating a plasma (P) by means of at least one plasma source (3) mounted on the process chamber (5) at a distance (L) from the substrate surface, at least part of the plasma (P) being injected into the chamber (5) and achieving a supersonic speed;
- contacting at least a part of the plasma (P), injected into the chamber (5), with the said part of the substrate surface; and
- supplying at least one precursor suitable for a-Si:H passivation layer realization to the said part of the plasma (P);
wherein the precursor is injected into the chamber via a number of injection nozzles, a lateral distance (R) between a centre line of the plasma and each injection nozzle being larger than 4 cm.

31. An apparatus for realizing at least one layer onto at least part of a surface of a substrate, the apparatus comprising:
- a process chamber (5), having a substrate holder for holding a substrate;
- at least one remote plasma source (3) mounted on the process chamber (5) at a distance from the substrate holder, for generating a plasma that expands into the chamber (5);
-an injector device for supplying at least one precursor suitable for layer realization to the expanding plasma (P);
wherein the injector device is provided with more than fifteen separate precursor injection nozzles.

32. An apparatus for realizing at least one layer onto at least part of a surface of a substrate, the apparatus comprising:
- a process chamber (5), having a substrate holder for holding a substrate;
- at least one remote plasma source (3) mounted on the process chamber (5) at a distance from the substrate holder, for generating a plasma that expands into the chamber (5);
-an injector device for supplying at least one precursor suitable for layer realization to the expanding plasma (P);

wherein the injector device is provided a number of nozzles, a total, cumulative, injection surface defined by the number of injection nozzles being larger than 10 mm^2.

33. A solar cell, provided with at least a part of a substrate at least obtained with a method according to any one of the claims 1-30.

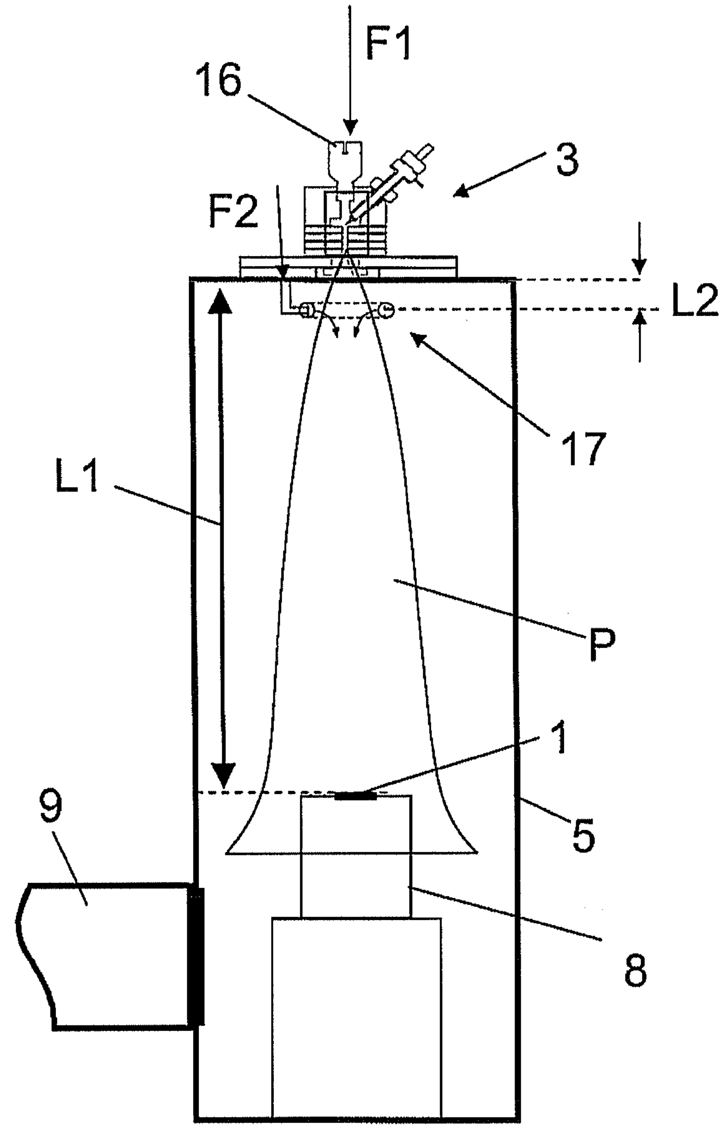

FIG.1

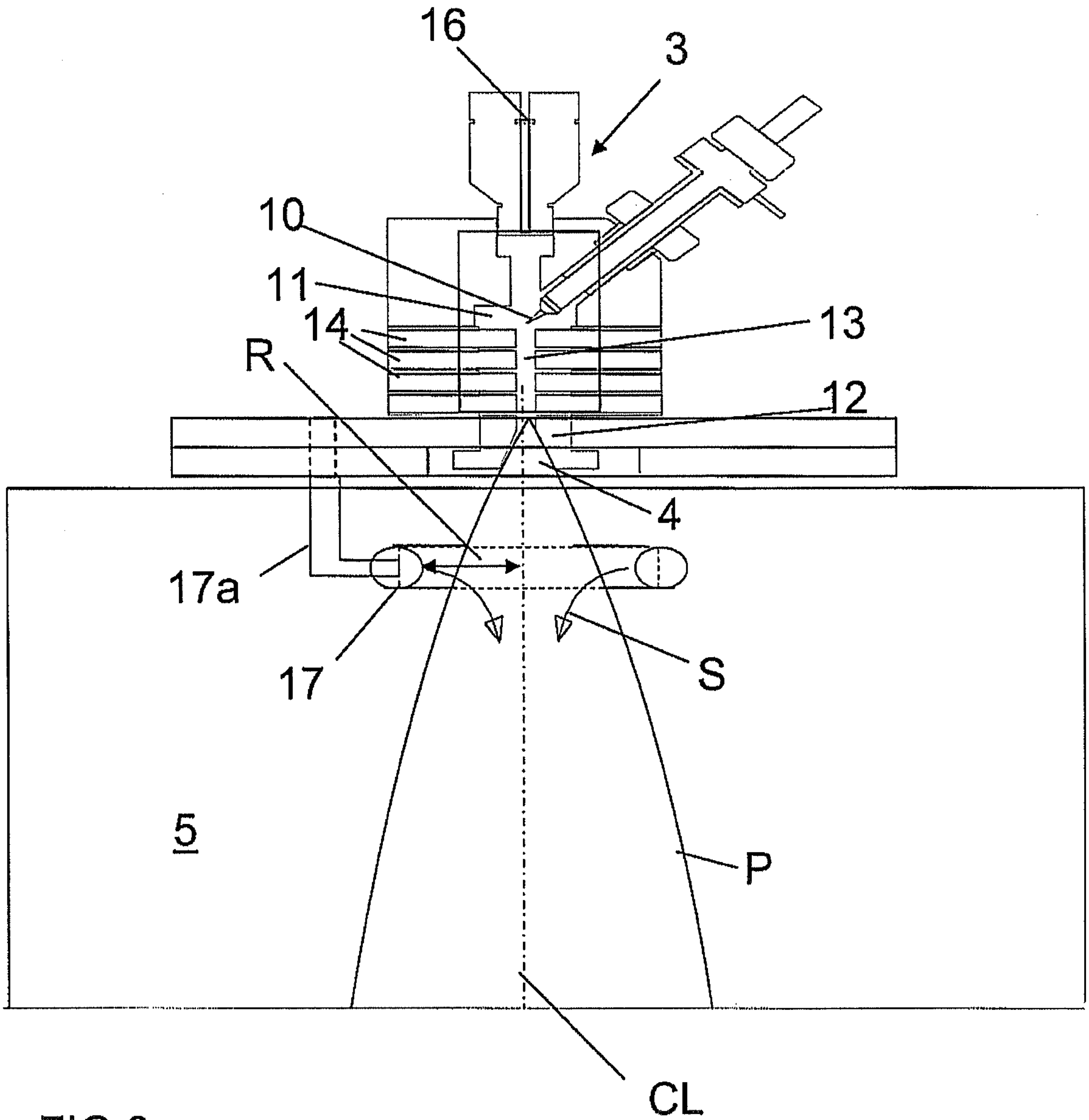

FIG.2

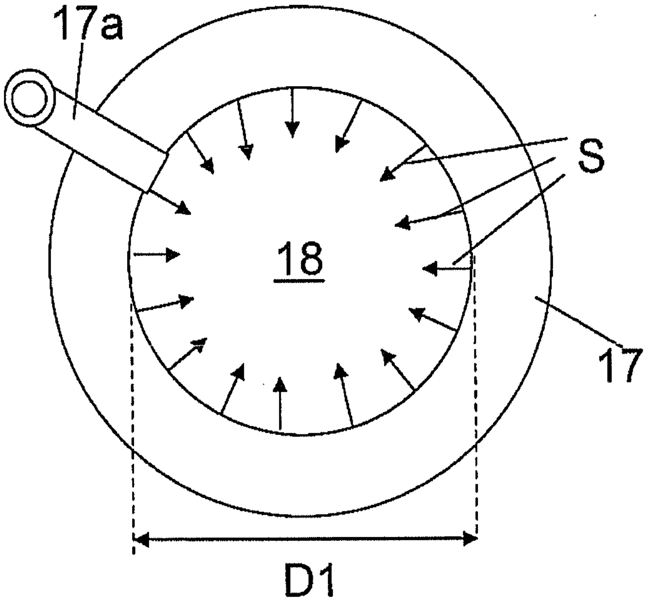

FIG.3

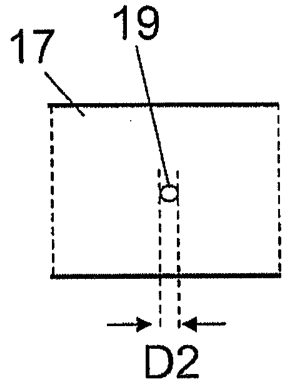

FIG.4

INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2010/050338

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C16/513 C23C16/455
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C

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

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

EPO-Internal, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KESSELS W M M ET AL: "High-rate deposition of a-SiNx:H for photovoltaic applications by the expanding thermal plasma" JOURNAL OF VACUUM SCIENCE AND TECHNOLOGY: PART A, AVS /AIP, MELVILLE, NY., US, vol. 20, no. 5, 1 September 2002 (2002-09-01), pages 1704-1715, XP012006185 ISSN: 0734-2101 page 1706 -----	1-32

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document 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
14 September 2010	28/09/2010

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

INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2010/050338

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HOEX B ET AL: "High-Quality Surface Passivation Obtained by High-Rate Deposited Silicon Nitride, Silicon Dioxide and Amorphous Silicon using the Versatile Expanding Thermal Plasma Technique" PHOTOVOLTAIC ENERGY CONVERSION, CONFERENCE RECORD OF THE 2006 IEEE 4TH WORLD CONFERENCE ON, IEEE, PI, 1 May 2006 (2006-05-01), pages 1036-1039, XP031007484 ISBN: 978-1-4244-0016-4	33
Y	page 1038, left-hand column, paragraph 4 - right-hand column, paragraph 2 * abstract	1-32
A	VAN ERVEN A J M ET AL: "Textured silicon surface passivation by high-rate expanding thermal plasma deposited SiN and thermal SiO2/SiN stacks for crystalline silicon solar cells" PROGRESS IN PHOTOVOLTAICS: RESEARCH AND APPLICATIONS JOHN WILEY & SONS LTD. UK, vol. 16, no. 7, November 2008 (2008-11), pages 615-627, XP002565068 ISSN: 1062-7995 * abstract	1-33
A	US 2006/231031 A1 (DINGS FRANCISCUS C [NL] ET AL DINGS FRANCISCUS CORNELIUS [NL] ET AL) 19 October 2006 (2006-10-19) the whole document	1-33
A	Hoex B, Kessels W M M, Bijker M D, van de Sanden M C M: "State of the art surface passivation by hydrogenated amorphous silicon deposited at rates >1nm/s by the expanding thermal plasma technique" In: "Proceedings of the 21st European PVSEC, Dresden, 2006" 8 September 2006 (2006-09-08), , XP002600585 , page 435 cited in the application the whole document	1-33

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/NL2010/050338

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