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(54) Title: PASSIVATION OF SILICON DIELECTRIC INTERFACE

(57) Abstract: A process for passivating the silicon / dielectric interface of a silicon wafer coated with a dielectric layer suitable for use in photovoltaic cells which convert energy from light impinging on the front face of the cell into electrical energy.

PASSIVATION OF SILICON DIELECTRIC INTERFACE

[0001] This invention relates to a process for passivating the silicon / dielectric interface of a silicon wafer coated with a dielectric layer. It is particularly concerned with silicon wafers coated with dielectric suitable for use in photovoltaic cells which convert energy from light impinging on the front face of the cell into electrical energy. (The front face of a photovoltaic cell is the major surface facing the light source and the opposite major surface is the back surface). Passivating the silicon/dielectric interface increases the conversion efficiency of a photovoltaic device, for example a solar cell, made from the silicon wafer coated with dielectric.

[0002] Photovoltaic devices or solar cells are typically configured as a cooperating sandwich of p- and n-type semiconductors, wherein the n-type semiconductor material exhibits an excess of electrons, and the p-type semiconductor material exhibits an excess of holes. Such a structure, when appropriately located electrical contacts are included, forms a working photovoltaic cell. Sunlight incident on photovoltaic cells is absorbed in the p-type semiconductor creating electron/hole pairs. By way of a natural internal electric field created by sandwiching p- and n-type semiconductors, electrons created in the p-type material flow to the n-type material where they are collected, resulting in a DC current flow between the opposite sides of the structure when the same is employed within an appropriate, closed electrical circuit.

[0003] Photovoltaic cells are widely used as solar cells for providing electricity from impinging sunlight. Significant cost reduction of silicon solar cells requires a high throughput, low cost, and reliable industrial process on thin silicon wafer substrates. The thickness of the silicon wafer processed in mass production of solar cells has progressively decreased and is now about 180μm; it is expected to be about 100 μm by 2020. This imposes significant modifications to the architecture of the solar cell because of cell bowing and loss of conversion efficiency. Cell bowing may result from a mismatch of the coefficients of thermal expansion of materials used in the cell. Loss in conversion efficiency may result from the larger number of photo-generated minority carriers reaching the back of thinner cells during their lifetime and being subject to back surface recombination through interfacial defects.

[0004] Present industrial surface conditioning and back surface passivation processes do not meet the requirements for yield and performance on thin substrates. The currently dominating technology of Aluminium Back Surface Field (Al-BSF) cell architecture, has reached its limits, particularly because of excessive cell bowing with wafers below about 200 μm following the high temperature (800℃+) co-firing step generally used in solar cell production. Alternatives are required, particularly for back surface passivation. The Al-BSF

cell architecture also suffers from poor reflection for red/IR photons. The rear side reflectivity of an Al-BSF solar cell reaches only 65% and is particularly poor above 1000nm.

[0005] One alternative solution relies on the use of dielectric layers for the passivation of the back surface, at least one of the layers of the stack being hydrogen rich to be used as a hydrogen source for dangling bonds passivation.

[0006] A paper by M. Tucci et al in Thin Solid Films (2008), 516(20), pages 6939-6942 describes thermal annealing after the sequential deposition by plasma enhanced chemical vapour deposition (PECVD) of a stack of hydrogenated amorphous silicon and hydrogenated amorphous silicon nitride to ensure stable passivation.

[0007] WO-A-2007/055484 and WO-A-2008/07828 disclose an alternative stack made of a silicon oxy-nitride (SiOxNy) passivation layer and a silicon nitride anti-reflective layer deposited on the back of the cell for surface passivation and optical trapping. The passivation layer is 10-50nm thick while the anti reflective layer is 50-100nm thick.

[0008] WO-A-2006/110048 (US-A-2009/056800) discloses the deposition of a thin hydrogenated amorphous silicon or hydrogenated amorphous silicon carbide film, followed by the deposition of a thin hydrogenated silicon nitride film, preferably by PECVD (Plasma Enhanced Chemical vapour deposition) prior to a final anneal at high temperature in forming gas.

[0009] US-A-2010/0323503 describes depositing a thin (0.1 to 10nm) amorphous hydrogenated silicon layer on the surface to be passivated and converting it to SiO2 by rapid thermal processing in an oxygen environment at between 750°C and 1200°C for 5 seconds to 30 minutes.

[0010] WO-A-2006/097303 and US-A-2009/0301557 describe a method for the production of a photovoltaic device, for instance a solar cell, by depositing a dielectric layer on the rear surface of a semiconductor substrate and depositing a passivation layer comprising hydrogenated silicon nitride on top of the dielectric layer and forming back contacts through the dielectric layer and the passivation layer.

[0011] A process according to one aspect of the present invention for passivating the silicon / dielectric interface of a silicon wafer coated with a dielectric layer comprises the steps of:

(i) coating the dielectric surface with a silicon-containing polymer containing Si-H groups and

(ii) heating the resulting coated wafer at a temperature in the range 470°C to 620°C in an inert atmosphere.

[0012] A process for passivating the silicon / dielectric interface of a silicon wafer coated with a dielectric layer according to another aspect of the invention comprises the steps of:

(i)(a) coating the dielectric surface with a silicon-containing polymer containing Si-H groups,

(i)(b) overcoating the siloxane resin with a layer of aluminium and

(ii) heating the resulting coated wafer at a temperature in the range 470°C to 1020°C in an inert atmosphere.

[0013] The silicon-containing polymer containing Si-H groups is an effective agent for hydrogenating the dielectric layer, thus achieving excellent passivation of the silicon dielectric interface. The excellent passivation by the process of the present invention is demonstrated by the low surface recombination velocity (lower than 300cm/s) and the high minority carrier lifetime (longer than 50µs). The silicon-containing polymer containing Si-H groups also has a refractive index after heating equal to or lower than the refractive index of typical dielectric layers, which may be important in achieving good rear side reflectivity.

[0014] The invention includes a photovoltaic device comprising a silicon wafer coated with a dielectric layer that is overcoated with a silicon-containing polymer containing Si-H groups and passivated by heating according to the process described above.

[0015] The silicon wafer substrate which is coated is generally crystalline and can be mono-crystalline or multi-crystalline silicon. A mono-crystalline wafer can for example be a float-zone (FZ) silicon wafer, a Czochralski process (CZ) silicon wafer or a quasi-mono type silicon wafer. The silicon wafer can for example be 100 µm to 400 µm thick (provided in the specification from the wafer manufacturer). An example of a preferred silicon wafer is a FZ wafer of bulk lifetime greater than 500 µs and resistivity 1-5 Ω.cm. The wafer may have both faces, one face or none of its faces chemically polished. The non-polished surfaces are preferably textured.

[0016] The dielectric layer that is coated on the silicon wafer is preferably a silicon dioxide layer or can alternatively be an aluminium oxide layer. This dielectric oxide layer can in general be formed by any method.

[0017] A silicon dioxide layer can for example be formed by thermal oxidation (oxidation of the surface of the silicon wafer), low pressure chemical vapour deposition, a sol-gel process, sputtering, or a plasma process such as plasma enhanced chemical vapour deposition or deposition from a non-local thermal equilibrium atmospheric pressure plasma. The silicon dioxide layer can be formed by oxidation of a precursor silicon compound, for example by heating in an oxygen-containing atmosphere. For example an organosilicon precursor

compound or polymer can be deposited on the silicon wafer by coating from solution or by deposition from a plasma and can be oxidised to a silicon dioxide layer. One example is a hydrogen silsesquioxane resin applied by coating from solution. Alternatively a silicon carbon oxide can be deposited from a plasma into which an organosilicon compound such as a low molecular weight linear siloxane or cyclosiloxane, or an alkoxysilane such as tetraethoxysilane, is introduced. A suitable apparatus for carrying out this process using a non-local thermal equilibrium atmospheric pressure plasma is described in WO-A-2012/003624.

[0018] An aluminium oxide can be formed by atomic layer deposition (ALD), by sputtering, sol-gel process or pyrolysis in an oxidizing atmosphere of an aluminium-based precursor.

[0019] The silicon-containing polymer containing Si-H groups is preferably a siloxane resin. One example of a siloxane resin is hydrogen silsesquioxane resin. Hydrogen silsesquioxane resin is a silicone resin substantially of the empirical formula $HSiO_{3/2}$. It can be prepared by the hydrolysis of trichlorosilane $HSiCl_3$. The hydrogen silsesquioxane resin generally has a cage-like molecular structure. Alternatively the siloxane resin containing Si-H groups can be a silicone resin containing hydrocarbyl groups bonded to silicon, for example $Si-CH_3$ groups, in addition to Si-H groups. The hydrogen silsesquioxane resin or other siloxane resin containing Si-H groups can be used alone or can be blended with another silicon-containing polymer, for example with a silsesquioxane resin such as methyl silsesquioxane resin of empirical formula $CH_3SiO_{3/2}$. The Si-H groups preferably form at least 40 mole% of the total organic and hydrogen groups bonded to silicon in the silicon-containing polymer containing Si-H groups.

[0020] The silicon-containing polymer can alternatively be an organopolysiloxane containing $RHSiO_{2/2}$ siloxane units where R represents a hydrocarbyl group, preferably an alkyl group having 1 to 6 carbon atoms. The silicon-containing polymer can for example be a poly(methylhydrogensiloxane). Such an organopolysiloxane can if desired be blended with a siloxane resin containing Si-H groups, for example hydrogen silsesquioxane resin.

[0021] The silicon-containing polymer containing Si-H groups can alternatively be a perhydropolysilazane resin. Perhydropolysilazane has the empirical formula $(H_2Si-NH)_n$.

[0022] In step (i) of the process of the invention the dielectric layer of the silicon wafer coated with a dielectric layer is overcoated. It is preferably coated by applying a solution of the silicon-containing polymer, for example hydrogen silsesquioxane resin or other siloxane resin containing Si-H groups, to the dielectric layer. The solvent can then be evaporated from the coating of hydrogen silsesquioxane resin solution on the wafer. The solution of hydrogen silsesquioxane resin can for example be a solution in a volatile siloxane solvent

having a degree of polymerisation of less than 10 siloxane units per molecule such as hexamethyldisiloxane, octamethyltrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane and/or decamethyltetrasiloxane. The solution of hydrogen silsesquioxane resin can for example have a concentration of 1 to 50% by weight, alternatively 2 to 25%, for example a 25% solution of hydrogen silsesquioxane resin in a blend of hexamethyldisiloxane and octamethyltrisiloxane. This can be used without further dilution or can be diluted with a volatile siloxane solvent such as octamethyltrisiloxane and/or decamethyltetrasiloxane. The solution of hydrogen silsesquioxane resin can alternatively be a solution in an aliphatic ketone such as methyl isobutyl ketone, methyl ethyl ketone or methyl isoamyl ketone e.g. a 14% solution of hydrogen silsesquioxane resin in methyl isobutyl ketone. We have found that other silicon-containing polymers containing Si-H groups, for example siloxane resins containing Si-bonded hydrocarbyl groups or poly(methylhydrogen)siloxane, are generally soluble in the above solvents.

[0023] The solution of hydrogen silsesquioxane resin or other silicon-containing polymer containing Si-H groups can for example be applied to the silicon wafer by spin coating, slot die coating, spray coating such as ultra-sonic spray coating, dip coating, angle-dependent dip coating, flow coating, capillary coating, roll coating or tampon printing. Some of these methods are appropriate for the coating of a single side of the substrate at a time; others can be used for the simultaneous coating of both sides of the substrate. The most appropriate method may be selected depending upon the type of solar cell architecture required and the need for single-side or double-side coating. If both faces of the silicon wafer are coated with a dielectric layer, double-side coating is preferred; if only one face of the silicon wafer is coated with a dielectric layer, single-side coating is preferred.

[0024] The wafer is preferably coated in step (i) with an amount of silicon-containing polymer containing Si-H groups to produce a resin dry film thickness of 50nm to 1000nm, alternatively 100nm to 500nm.

[0025] The spin coating process consists in dispensing a defined volume of solution on a substrate that is, or will be, submitted to spinning. The silicon wafer substrate coated with a dielectric layer is placed on a chuck, made of aluminium or Teflon, in a spin coater such as that sold by Chemat Technology as model KW-4A and held in place by vacuum suction. The silicon-containing polymer, for example hydrogen silsesquioxane resin, solution can be dispensed in static mode (the substrate not spinning during the dispensing stage) or in dynamic mode (the substrate is subject to low speed spinning while dispensing the solution). The spinning process consists of first spinning the substrate at low speed (200-600rpm) for a short time (2-10s) and then spinning the substrate at high rate (1000-10000rpm) for a longer

time (10s-60s) to spread the solution evenly over the wafer substrate. The thickness of the resulting coating will depend upon the solid content of the resin solution and the spinning rate during the second spinning step. Coatings of dry film thickness in the range 40 to 500nm are generally produced from hydrogen silsesquioxane resin solutions of concentration in the range 5 to 25% by weight. The spin coating process has the advantage of providing a very homogeneous coating in terms of thickness, with thickness variation typically in the <±1% to ±6%, although it has the disadvantages of long duration time and low product usage.

[0026] Spray coating is a suitable process for overcoating the silicon wafer coated with a dielectric layer. An example of a suitable spray nozzle is a Burgener ARI MIST HP Serial 14.547 nebulizer. The coating solution of silicon-containing polymer containing Si-H groups can be deposited by scanning the wafer with the nebulized spray. Spraying has the advantage of relatively high coating rate while producing a homogeneous coating (±8%). A relatively dilute solution is preferred for spraying, for example a 4-10% by weight solution of hydrogen silsesquioxane resin.

[0027] Slot die coating is another suitable process for overcoating the dielectric layer on the silicon wafer substrate with the silicon-containing polymer containing Si-H groups. In the slot die process, the coating is squeezed out by gravity or under pressure through a slot and onto the substrate. The slot-die coater is a pre-metered coating method in which a precision pump delivers the coating solution to the slot die so that all of the coating solution metered to the die is applied to the web. Slot die coating also has the advantages of extremely high thickness homogeneity (<±3 %) and a relatively high coating rate. A relatively dilute solution is preferred for slot die coating, for example a 1-5% by weight solution of hydrogen silsesquioxane resin depending upon the thickness to achieve and the precision of the pumping system.

[0028] The solvent can be evaporated from the coating of hydrogen silsesquioxane resin or other silicon-containing polymer solution at ambient temperature or at elevated temperature. In one preferred process according to the invention the wafer coated with hydrogen silsesquioxane resin is heated at a temperature of 50℃ to 350℃ to partially crosslink the silsesquioxane resin before the thermal treatment step (ii). The crosslinking, sometimes called 'curing' consists in the siloxane bond rearrangement from a cage-like structure to a network structure with no or little loss of the SiH groups. Heating can be carried out with a gradual or stepwise increase in temperature, for example 2 minutes each at 150℃, 200℃ and then 350℃, or can be at a single temperature, for example 6 minutes at 150℃. The purpose of the partial crosslinking step is to build a three dimensional network

with mechanical integrity and stability for subsequent processing. Such a partial crosslinking step can be carried out in an oxidative, reducing or inert atmosphere.

[0029] If the dielectric layer is a silicon dioxide layer formed by application of a hydrogen silsesquioxane resin to the silicon wafer and oxidation of the hydrogen silsesquioxane resin to a silicon dioxide layer, the hydrogen silsesquioxane resin can be coated on the silicon wafer and heated to evaporate solvent and optionally to partially crosslink the silsesquioxane resin as described above. The hydrogen silsesquioxane resin coating can be thermally treated to oxidise the hydrogen silsesquioxane resin layer into a silicon dioxide dielectric layer. In this thermal treatment, the hydrogen silsesquioxane resin coating is subjected to a temperature above 350°C for 5 to 120 seconds. During this treatment the hydrogen silsesquioxane resin is subject to a maximum temperature in the range 700°C to 1020°C. This short time high temperature treatment can for example be achieved using an in-line furnace of the type used by the photovoltaic industry for the thermal contact annealing step of solar cell fabrication. The thermal treatment step is preferably carried out in an oxygen-containing atmosphere, for example air.

[0030] The layer of silicon-containing polymer containing Si-H groups coated over the dielectric layer is heated at a temperature in the range 470°C to 620°C in an inert atmosphere. This causes release of hydrogen from the siloxane resin containing Si-H groups and hydrogenation of the silicon/dielectric layer interface, resulting in passivation of the silicon/dielectric interface. Only a short time of heating is necessary, for example 5 to 120 seconds, alternatively 10 to 40 seconds, at above 300°C. The time for which the silicon-containing polymer containing Si-H groups is exposed to a temperature above 450ºC is preferably in the range 0.5 to 10 seconds. We have found that optimal passivation is achieved when heating at 470°C to 620°C (maximum temperature); heating at a higher or lower temperature does not give such good passivation. This moderate temperature range may be advantageous for temperature sensitive devices.

[0031] The inert atmosphere is preferably a nitrogen atmosphere. An atmosphere of a noble gas such as argon can be used but is not necessary. Hydrogen can be present in the nitrogen atmosphere to give an additional hydrogen source for hydrogenation, but this is not necessary. The nitrogen atmosphere can for example contain up to 20% by volume hydrogen, particularly 2 to 20% or alternatively 5 to 10% by volume hydrogen.

[0032] Passivation can for example be measured by calculating the minority carrier lifetime using a μ-PCD (microwave detected photoconductive decay) device. The minority carrier lifetime is measured after hydrogenation without formation of back contacts. Increased minority carrier lifetime shows improved passivation. A suitable μ-PCD device is for example

supplied by SemiLab under the trade mark WT-2000. In the μ-PCD technique, a microwave antenna is placed near the surface of the wafer to direct microwaves at its surface. Some of the microwave signal will enter the semiconductor and another portion will be reflected, depending upon the conductivity of the sample. The wafer conductivity will be modified by means of a laser light pulse that will affect the concentration of the minority carrier and will modify the portion of the reflected microwaves. The time evolution of this portion will be followed as the excess minority carrier decreases and the wafer conductivity comes back to its equilibrium value. The exponential signal decays as a function of the lifetime of the minority carriers and allows determination of the surface recombination rate. A minority carrier lifetime longer than 50μs indicates effective passivation.

[0033] Another measure of surface passivation is the effective surface recombination velocity S_{eff}.

[0034] In a doped silicon wafer, used to make a solar cell, some carriers are in excess compared to others. For example in a p-type Si wafer the dopant (typically boron) adds "holes" to the electrical charges resulting in electrons being the minority carriers. However, in the case of a n-type wafer, the dopant e.g. phosphorus adds electrons to the electrical charges and hence the "holes" are the minority carriers.

[0035] Upon light absorption, electrons and holes are produced and due to the fact that either the electrons (p-type silicon) or the holes (n-type silicon) are the minority carriers, the rate of their recombination dictates the likelihood that they will be collected at an electrode, i.e. generate a current in an external circuit. In a "pure" wafer, these minority carriers recombine mostly at the surface of the wafer with majority carriers, due to the "catalytic" presence of defects at these surfaces. Hence, the rate of disappearance is directly linked to the surface recombination velocity. It is given by the following equation:

$$S_{eff} = \sqrt{D_n\left(\frac{1}{\tau_{eff}} - \frac{1}{\tau_{bulk}}\right) tan\left[\frac{W}{2}\sqrt{\frac{1}{D_n}\left(\frac{1}{\tau_{eff}} - \frac{1}{\tau_{bulk}}\right)}\right]}$$

where

D_n= charge carrier diffusion coefficient

τ_{eff} = effective minority carrier lifetime

τ_{bulk} = bulk minority carrier lifetime

W = wafer thickness

However, in the case of effective passivation, the surface recombination velocity is low and the equation can be simplified to

$$S_{eff} = \frac{W}{2}\left(\frac{1}{\tau_{eff}} - \frac{1}{\tau_{bulk}}\right)$$

The determination of the S_{eff} requires the knowledge of the τ_{bulk}. In experiments described in the present application, high quality silicon float-zone (FZ) wafers have been used with known bulk lifetime in excess of >500µs and a τ_{bulk} value of 2000µs (p-type FZ, double side mirror polished, resistivity 1-5Ω.cm). The effective surface recombination velocity, S_{eff}, should be as low as possible. It is considered that achieving a surface recombination velocity lower or equal to 300cm/s leads to very good passivation of the Si/dielectric interface.

[0036] In addition to improving passivation of the silicon dielectric interface, the silicon-containing polymer containing Si-H groups after heating at a temperature in the range 470°C to 620°C in an inert atmosphere has a refractive index very similar to that of the underlying dielectric layer, particularly if the dielectric layer is SiO_2. A hydrogen silsesquioxane resin layer thus heated, for example, has a refractive index matching quite precisely that of a dielectric layer of SiO_2. Such layer stack will act optically as a homogenous layer and provide optimal reflectivity in the red/IR range, a feature that is essential for solar cells made on thin wafers, for example those of thickness below 200µm.

[0037] The step of forming back contacts will generally be required when forming a solar cell. The formation of back contacts through dielectric layers is a known process. The formation of back contacts through silicon nitride and silicon dioxide layers is described for example in US-A-2009/0301557. Contacts are formed by forming holes in the dielectric silicon dioxide layer and depositing a layer of contacting material. The holes may be formed by laser ablation, by applying an etching paste, or by mechanical scribing. The layer of contacting material, for example a metal such as aluminium, can be deposited by evaporation, sputtering, screen printing, inkjet printing, or stencil printing. It can be deposited locally essentially in the holes or as a continuous or discontinuous layer. The holes can be formed before depositing the contacting material, so that the contacting material fills the holes. Alternatively the contacting material can be applied followed by opening the holes and making the contacts with a laser (laser-fired contacts). After the contacting material has been applied, the photovoltaic cell is generally subjected to a firing step. The firing step is preferably carried out at a temperature of at least 577°C (the Al-Si eutectic melts at 577°C) up to 620°C for 5 to 60 seconds The step of heating the layer of siloxane resin containing Si-H groups coated over the dielectric layer at a temperature in the range 470°C to 620°C in an inert atmosphere is thus followed by forming holes in the dielectric silicon dioxide layer and depositing a layer of contacting material, then firing at 577°C to 620°C.

[0038] Alternatively the holes can be opened with a laser in the layer of siloxane polymer containing Si-H groups and the contacting material such as aluminium metallization paste can be applied before the layer of siloxane polymer containing Si-H groups is heated in an inert atmosphere. The metallised layer can then be heated at a temperature in the range 470℃ to 620℃, alternatively 577℃ to 620℃, to achieve hydrogenation of the silicon/dielectric layer interface and firing of the contacts in a single heating step.

[0039] In an alternative procedure according to the invention, the layer of organosilicon polymer containing Si-H groups coated over the dielectric layer is overcoated with a layer of aluminium and then heated at a temperature in the range 470℃ to 1020℃ in an inert atmosphere. Heating is for a short time; for example 5 to 120 seconds, alternatively 10 to 40 seconds, at above 300℃. The time for which the silicon-containing polymer containing Si-H groups is exposed to a temperature above 450ºC is preferably in the range 1 to 10 seconds. Capping of the layer of organosilicon polymer containing Si-H groups, for example hydrogen silsesquioxane resin, with an aluminium layer gives some barrier properties against hydrogen escape, so that more hydrogen is released towards the silicon dielectric interface. This allows heating of the hydrogen silsesquioxane resin layer at a higher temperature. It also allows the use of a thinner layer of organosilicon polymer containing Si-H groups. If the layer of organosilicon polymer containing Si-H groups is not capped with aluminium, the layer of organosilicon polymer containing Si-H groups is preferably at least 100nm thick and passivation increases with the thickness of organosilicon polymer containing Si-H groups up to a thickness of about 200 or 300nm. Thicker layers are as effective. If the layer of organosilicon polymer containing Si-H groups is capped with aluminium, the layer of organosilicon polymer containing Si-H groups can be 100nm thick or even less, for example 50 to 100nm, and passivation is still achieved.

[0040] When the layer of organosilicon polymer containing Si-H groups coated over the dielectric layer is overcoated with a layer of aluminium, contacts can be formed by making holes through the aluminium layer, the layer of organosilicon polymer containing Si-H groups and the dielectric silicon dioxide layer, for example by laser ablation (laser fired contact technology). A single firing step, preferably at 600℃ to 1000℃, can then be used to simultaneously hydrogenate/passivate the silicon/dielectric silicon dioxide interface and to form contacts. The opening of the dielectric layer and the organosilicon polymer containing Si-H groups coated over the dielectric layer can be performed prior to applying the aluminum layer. Once the aluminum layer is applied the device can be submitted to a single firing step, preferably at 600℃ to 1000℃, to simultaneously hydrogenate/passivate the silicon/dielectric silicon dioxide interface and to form contacts.

[0041] The invention is illustrated by the following Examples, in which parts and percentages are by weight.

Example 1

[0042] 'A 25% solution of hydrogen silsesquioxane resin in a blend of hexamethyldisiloxane and octamethyltrisiloxanewas diluted with octamethyltrisiloxane to a resin concentration of 10.6%. 100mm diameter FZ silicon wafers were coated with the diluted resin solution in a Chemat Technology 'KW-4A' spin coater. 0.5ml of the resin solution was statically dispensed on the wafer substrate, and the substrate was spun for 6s at 300rpm and then for 20s at 2000rpm. This process was repeated on the other face of the silicon wafer so that the resin was coated on both faces with hydrogen silsesquioxane resin solution.

[0043] Solvent was eliminated from the hydrogen silsesquioxane resin solution, and the hydrogen silsesquioxane resin was cured by heating at 150℃ for 120s, then 200℃ for 120s, then 350℃ for 120s.

[0044] The resulting coated wafer was heated in air for a very short time in a SOLARIS 150 Rapid Thermal Processing system. The measured maximum temperature was 870℃ and the time at 850℃ or above was 2 seconds. The hydrogen silsesquioxane resin coating layers were converted to dielectric silicon dioxide layers 130nm thick having a refractive index of about 1.43. In the SSI Rapid Thermal Process (RTP) , the wafer is laid on a carrier made of quartz; a thermocouple is put in direct contact with the wafer and allows high accuracy temperature measurement; wafer is heat-up by two set of IR lamps facing the top and the bottom of the wafer. The IR lamps are computer controlled and the temperature as a function of time is recorded in-line using the signal of the thermocouple.

[0045] The resulting silicon wafer coated with dielectric layers was spin coated on both faces with the 10.6% hydrogen silsesquioxane resin solution described above. Solvent was eliminated from the hydrogen silsesquioxane resin solution, and the hydrogen silsesquioxane resin was cured, by heating at 150℃ for 120s, then 200℃ for 120s, then 350℃ for 120s. The dielectric layers were coated with hydrogen silsesquioxane resin layers each 170nm thick having a refractive index of 1.39.

[0046] The resulting coated wafer was heated in a nitrogen atmosphere at 580℃ (the time above 470℃ was 6 seconds) to passivate the silicon dielectric interface. The refractive index of the hydrogen silsesquioxane resin layers after heating was 1.42, so that the hydrogen silsesquioxane resin silicon dielectric composite looks like a homogeneous SiO2 layer that provides the best reflection in the red/IR range

[0047] The minority carrier lifetime measured using a SemiLab WT-2000 μ-PCD device was 110μs. The effective surface recombination velocity S_{eff} was calculated as described above and was found to be 135cm/s.

Examples 2 and 3 and Comparative Example C1

[0048] Example 1 was repeated varying the temperature at which the coated wafer was heated in a nitrogen atmosphere. The temperatures used and the passivation achieved in terms of minority carrier lifetime and effective surface recombination velocity were measured as described in Example 1 are shown in Table 1.

Table 1

Example	Temperature	Time above 300 ºC (s)	Time above 450 ºC (s)	Lifetime μs	S_{eff} cm/s
1	583ºC	19	6.0	116	122
2	533ºC	18	4.8	74	198
3	471ºC	17	0.8	52	293
C1	678 ºC	22	8.2	18	836

Example 4

[0049] The apparatus of Figure 1 was used to deposit a layer of a silicon compound on a conductive silicon wafer substrate. The dielectric housing (14) defining the plasma tube (13) was 18mm in diameter. This housing (14) is made of quartz. The electrodes (11, 12) were each 1mm diameter and were connected to the Plasma Technics ETI110101 unit operated at 20kHz and maximum power of 100 watts. Helium process gas was flowed through chamber (19) and thence through channels (16, 17) at 2 slm. The channels (16, 17) were each 2mm in diameter, the electrodes (11, 12) being localized in the centre of each channel. The length of the channels was 30mm. The tip of each needle electrode (11, 12) was positioned close to the exit of the channel (16, 17 respectively) at a distance 0.5mm outside the channel exit.

[0050] The atomiser (21) was the Ari Mist HP pneumatic nebuliser supplied by Burgener Inc. Tetramethyltetracyclosiloxane was supplied to the atomiser (21) at 2 μl/m. Helium was fed to the atomiser (21) as atomising gas at 2.2slm. The gap (30) between quartz housing (14) and the silicon wafer substrate was 2 mm.

[0051] 4 inches (10cm) diameter Float Zone silicon circular wafers 350 nm thick were used to produce an assembly suitable for surface passivation measurement. Wafers were cleaned with a standard Pyrana recipe used in microelectronics followed by a 5 seconds dip in a 5%

by weight HF solution. Smooth organosilicon polymer films were deposited on both the top side and the rear side of the wafer.

[0052] The wafer was thermally treated in air by exposure of both silicon compound layers to contact firing at a maximum temperature of 850°C for 2 seconds. The time to reach maximum temperature was 6 seconds. The silicon compound layers were densified and converted to silicon oxide. The silicon oxide layers produced had no carbon content detectable by XPS. Each silicon oxide layer was ~ 250 nm thick.

[0053] The resulting silicon wafer coated with dielectric layers was spin coated on both faces with 25% hydrogen silsesquioxane resin solution as described in Example 1. Solvent was eliminated and the hydrogen silsesquioxane resin was cured as described in Example 1. Each dielectric layer was thus coated with a 450nm layer of hydrogen silsesquioxane resin.

[0054] The coated wafer thus produced was heated in a nitrogen atmosphere at 580°C and the time above 470°C was 6 seconds to passivate the silicon dielectric interface. The minority carrier lifetime measured using a SemiLab WT-2000 μ-PCD device was 220μs. The effective surface recombination velocity S_{eff} was calculated and is shown in Table 2.

Examples 5 to 7

[0055] Example 4 was repeated with the variation that the 25% solution of hydrogen silsesquioxane resin in a blend of hexamethyldisiloxane and octamethyltrisiloxane was diluted with octamethyltrisiloxane to form resin solutions of various concentrations as shown in Table 2. The thickness of the cured hydrogen silsesquioxane resin coatings was dependent on the resin solution concentration and is shown in Table 2. For each Example the minority carrier lifetime was measured after passivation by heating in nitrogen and the effective surface recombination velocity S_{eff} was calculated; these are shown in Table 2.

Table 2

Example	Resin solution concentration	Resin coating thickness nm	Minority carrier lifetime μs	S_{eff} cm/s
4	25%	450	195	69
5	8%	120	76	193
6	12%	200	125	113
7	16%	290	197	68

[0056] It can be seen from Table 2 that excellent passivation is achieved in Example 5 with a 120nm thick hydrogen silsesquioxane resin coating, and that even better results are obtained in Examples 4, 6 and 7 using thicker coatings.

[00575] The invention may be any one of the following numbered aspects:

1. A process for passivating the silicon / dielectric interface of a silicon wafer coated with a dielectric layer, comprising the steps of:-
   (i) coating the dielectric surface with a silicon-containing polymer containing Si-H groups and
   (ii) heating the resulting coated wafer at a temperature in the range 470℃ to 620℃ in an inert atmosphere.
2. A process for passivating the silicon / dielectric interface of a silicon wafer coated with a dielectric layer, comprising the steps of:-
   (i)(a) coating the dielectric surface with a silicon-containing polymer containing Si-H groups,
   (i)(b) overcoating the siloxane resin with a layer of aluminium and
   (ii) heating the resulting coated wafer at a temperature in the range 470℃ to 1020℃ in an inert atmosphere
3. A process according to Aspect 1 or Aspect 2 wherein the dielectric layer is a silicon dioxide layer.
4. A process according to Aspect 1 or Aspect 2 wherein the dielectric layer is an aluminium oxide layer.
5. A process according to any of Aspects 1 to 4 wherein the silicon-containing polymer is a siloxane resin.
6. A process according to Aspect 5 wherein the siloxane resin comprises hydrogen silsesquioxane.
7. A process according to Aspect 6 wherein the siloxane resin is a mixture of hydrogen silsesquioxane with another silsesquioxane resin.
8. A process according to Aspect 5 wherein the siloxane resin comprises Si-H groups and Si- bonded hydrocarbyl groups.
9. A process according to any of Aspects 1 to 4 wherein the silicon-containing polymer is an organopolysiloxane containing RHSiO2/2 siloxane units where R represents a hydrocarbyl group.
10. A process according to Aspect 9 wherein the organopolysiloxane is a poly(methylhydrogensiloxane).
11. A process according to any of Aspects 1 to 5 wherein the silicon-containing polymer comprises perhydropolysilazane.
12. A process according to any of Aspects 1 to 7 wherein in step (i) the dielectric surface is coated by applying a solution of the silicon-containing polymer to the

dielectric surface and the coated surface is subsequently heated at a temperature of 50°C to 350°C to evaporate the solvent.

13. A process according to Aspect 12 wherein the solution is a solution of a hydrogen silsesquioxane resin in a volatile siloxane solvent having a degree of polymerisation of less than 10 siloxane units per molecule.

14. A process according to Aspect 12 or Aspect 13 wherein the solution of siloxane resin is applied to the dielectric surface by spin coating or slot die coating.

15. A process according to any of Aspects 1 to 14 wherein in step (ii) the time for which the silicon-containing polymer containing Si-H groups is exposed to a temperature above 450ºC is in the range 0.5 to 10 seconds.

16. A process according to any of Aspects 1 to 15 wherein in step (ii) the coated wafer is heated in a nitrogen atmosphere.

17. A process according to Aspect 16 wherein the nitrogen atmosphere contains 2 to 20% by volume hydrogen.

18. A process according to any of Aspects 1 to 17 wherein in step (i) the amount of silicon-containing polymer coated on the dielectric surface is such that after step (ii) the thickness of the silicon-containing polymer layer is 100nm to 1000nm.

19. A process for passivating the silicon / dielectric interfaces of a silicon wafer coated with a dielectric layer on both faces, wherein both dielectric surfaces are coated with a silicon-containing polymer containing Si-H groups and heated according to any of Aspects 1 to 18.

20. A process for the production of a photovoltaic device, wherein a silicon wafer coated with a dielectric layer is overcoated with a silicon-containing polymer containing Si-H groups and passivated by heating according to any of Aspects 1 to 19, contacts are formed by forming holes in the dielectric layer and depositing a layer of contacting material, and the contacts are fired at a temperature in the range 577°C to 620°C.

21. A process for the production of a photovoltaic device, wherein a silicon wafer coated with a dielectric layer is overcoated with a silicon-containing polymer containing Si-H groups, contacts are formed by forming holes in the dielectric layer and depositing a layer of contacting material, and the product is heated according to any of Aspects 1 to 19 to passivate the silicon/dielectric layer interface and to fire the contacts.

22. A photovoltaic device comprising a silicon wafer coated with a dielectric layer that is overcoated with a silicon-containing polymer containing Si-H groups and passivated by heating according to any of Aspects 1 to 19.

CLAIMS

1. A process for passivating the silicon / dielectric interface of a silicon wafer coated with a dielectric layer, comprising the steps of:-
   (iii) coating the dielectric surface with a silicon-containing polymer containing Si-H groups and
   (iv) heating the resulting coated wafer at a temperature in the range 470℃ to 620℃ in an inert atmosphere.

2. A process for passivating the silicon / dielectric interface of a silicon wafer coated with a dielectric layer, comprising the steps of:-
   (i)(a) coating the dielectric surface with a silicon-containing polymer containing Si-H groups,
   (i)(b) overcoating the siloxane resin with a layer of aluminium and
   (ii) heating the resulting coated wafer at a temperature in the range 470℃ to 1020℃ in an inert atmosphere

3. A process according to Claim 1 or Claim 2 wherein the dielectric layer is a silicon dioxide layer; or wherein the dielectric layer is an aluminium oxide layer.

4. A process according to any one of Claims 1 to 3 wherein the silicon-containing polymer is a siloxane resin; or wherein the silicon-containing polymer is a siloxane resin wherein the siloxane resin comprises hydrogen silsesquioxane; or wherein the silicon-containing polymer is a siloxane resin wherein the siloxane resin is a mixture of hydrogen silsesquioxane with another silsesquioxane resin; or wherein the silicon-containing polymer is a siloxane resin wherein the siloxane resin comprises Si-H groups and Si- bonded hydrocarbyl groups.

5. A process according to any one of Claims 1 to 3 wherein the silicon-containing polymer is an organopolysiloxane containing RHSiO2/2 siloxane units where R represents a hydrocarbyl group; or wherein the silicon-containing polymer is an organopolysiloxane containing RHSiO2/2 siloxane units where R represents a hydrocarbyl group wherein the organopolysiloxane is a poly(methylhydrogensiloxane).

6. A process according to any one of Claims 1 to 3 wherein the silicon-containing polymer comprises perhydropolysilazane.

7. A process according to any one of Claims 1 to 3 wherein in step (i) the dielectric surface is coated by applying a solution of the silicon-containing polymer to the dielectric surface and the coated surface is subsequently heated at a temperature of 50℃ to 350℃ to evaporate the solvent.

8. A process according to Claim 7 wherein the solution is a solution of a hydrogen silsesquioxane resin in a volatile siloxane solvent having a degree of polymerisation of less than 10 siloxane units per molecule; wherein the solution of siloxane resin is applied to the dielectric surface by spin coating or slot die coating; or wherein the solution is a solution of a hydrogen silsesquioxane resin in a volatile siloxane solvent having a degree of polymerisation of less than 10 siloxane units per molecule and wherein the solution of siloxane resin is applied to the dielectric surface by spin coating or slot die coating.

9. A process according to any one of Claims 1 to 8 wherein in step (ii) the time for which the silicon-containing polymer containing Si-H groups is exposed to a temperature above 450ºC is in the range 0.5 to 10 seconds.

10. A process according to any one of Claims 1 to 9 wherein in step (ii) the coated wafer is heated in a nitrogen atmosphere; or wherein in step (ii) the coated wafer is heated in a nitrogen atmosphere and the nitrogen atmosphere contains 2 to 20% by volume hydrogen.

11. A process according to any one of Claims 1 to 10 wherein in step (i) the amount of silicon-containing polymer coated on the dielectric surface is such that after step (ii) the thickness of the silicon-containing polymer layer is 100nm to 1000nm.

12. A process for passivating the silicon / dielectric interfaces of a silicon wafer coated with a dielectric layer on both faces, wherein both dielectric surfaces are coated with a silicon-containing polymer containing Si-H groups and heated according to any one of Claims 1 to 11.

13. A process for the production of a photovoltaic device, wherein a silicon wafer coated with a dielectric layer is overcoated with a silicon-containing polymer containing Si-H groups and passivated by heating according to any one of Claims 1 to 12, contacts are formed by forming holes in the dielectric layer and depositing a layer of contacting material, and the contacts are fired at a temperature in the range 577℃ to 620℃.

14. A process for the production of a photovoltaic device, wherein a silicon wafer coated with a dielectric layer is overcoated with a silicon-containing polymer containing Si-H groups, contacts are formed by forming holes in the dielectric layer and depositing a layer of contacting material, and the product is heated according to any one of Claims 1 to 12 to passivate the silicon/dielectric layer interface and to fire the contacts.

15. A photovoltaic device comprising a silicon wafer coated with a dielectric layer that is overcoated with a silicon-containing polymer containing Si-H groups and passivated by heating according to any of Claims 1 to 12.

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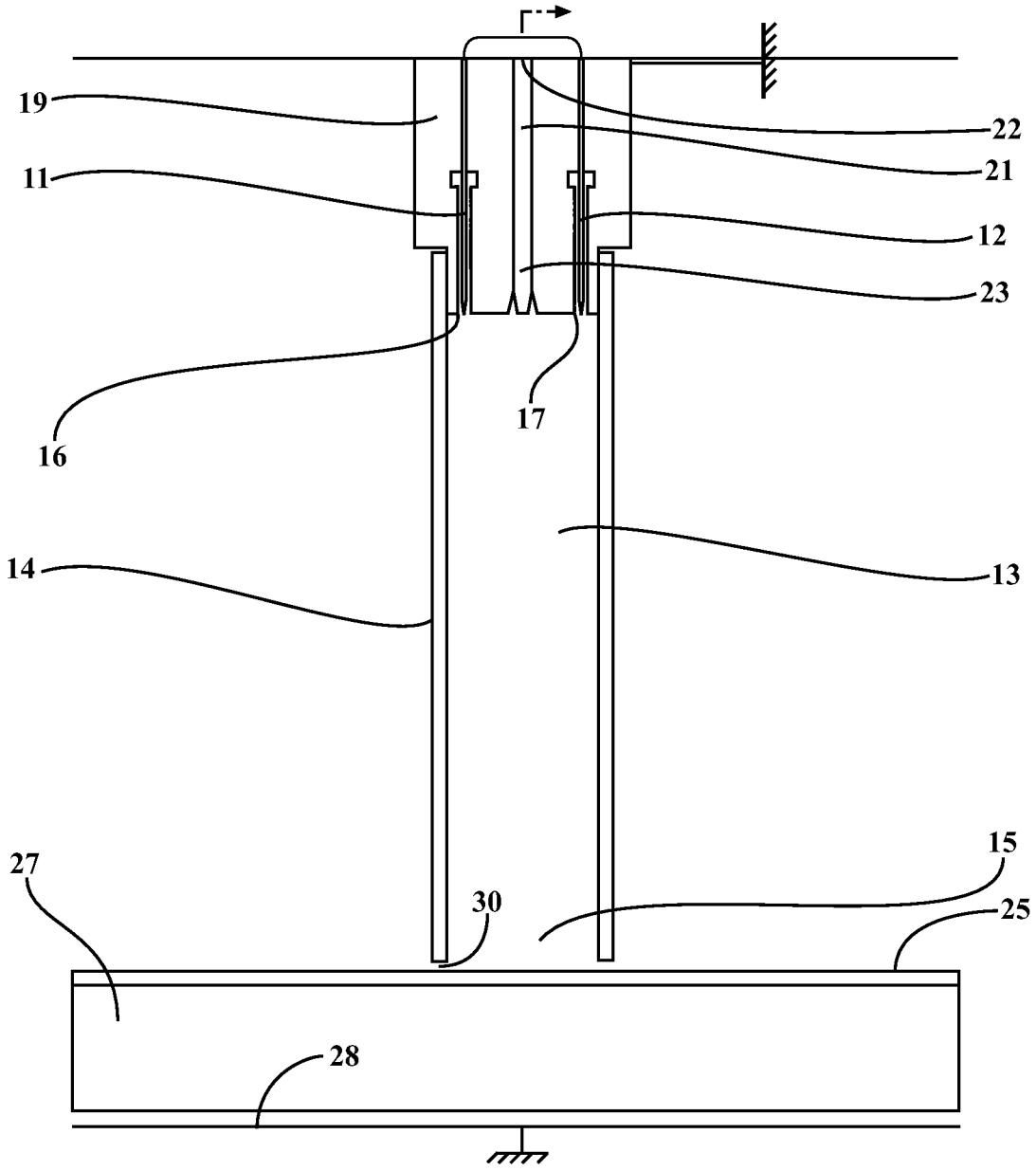


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/038101

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01L31/0216 H01L31/18
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)
H01L

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 practicable, search terms used)
EPO-Internal, WPI Data, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2005 026534 A (SHARP KK) 27 January 2005 (2005-01-27) abstract paragraphs [0029], [0041], [0047], [0052] paragraph [0035] - paragraph [0036]; figure 4 paragraph [0075] - paragraph [0078]; figures 13(a)-13(e) -----	1
X	US 2002/045339 A1 (YAMAHA TAKAHISA [JP]) 18 April 2002 (2002-04-18) abstract paragraph [0041] - paragraph [0090]; figures 3,5 -----	1,2
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
15 October 2013	05/11/2013

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/038101

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 980 091 A2 (TEXAS INSTRUMENTS INC [US]) 16 February 2000 (2000-02-16) paragraphs [0001], [0006], [0013], [0015] - [0017]; figures 1,3 -----	1
A	WO 2006/097303 A1 (IMEC INTER UNI MICRO ELECTR [BE]; AGOSTINELLI GUIDO [BE]; BEAUCARNE GU) 21 September 2006 (2006-09-21) cited in the application abstract page 19, line 20 - page 23, line 16 page 24, line 12 - line 20 figures 1-3 -----	1-15

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Information on patent family members

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