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(54) METHOD FOR THE WET-CHEMICAL ETCHING OF A HIGHLY DOPED SEMICONDUCTOR LAYER

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(57) ABSTRACT

A method for the wet-chemical etching of a silicon layer in an alkaline etching solution is provided, where the silicon layer is the surface region of a solar cell emitter. The method ensures that the surface region of the emitter is etched-back homogeneously using an oxidant-free alkaline etching solution comprising at least one organic moderator is used for the isotropic etching back of the surface region of the emitter, where the moderator has a dopant concentration of at least 10^{18} atoms/cm^3.

METHOD FOR THE WET-CHEMICAL ETCHING OF A HIGHLY DOPED SEMICONDUCTOR LAYER

[0001] The invention relates to a method for the wet-chemical etching of a silicon layer in an alkaline etching solution, the silicon layer being the surface region of a solar cell emitter.

[0002] The quality factor/structure of an emitter is one of the crucial factors for the efficiency of a solar cell. The emitter depth, the dopant profile, the surface concentration of the dopant, and the emitter layer resistance must be precisely adjusted to obtain optimal cell properties.

[0003] The emitter properties are influenced by the diffusion parameters of temperature and time as well as the type of doping agent. In the framework of economically applicable industrial processes, however, it is not possible to adjust all properties at will and independently of one another.

[0004] In the currently widespread methods for producing crystalline solar cells, homogeneously doped mono- and multicrystalline p-type silicon wafers, usually with boron base doping, are used as starting materials. The concentration of the dopant is on the order of 10^{16} atoms/cm^3. The emitter is produced by in-diffusion of phosphorus. The most important target parameter, which is readily accessible by measurement technology, is the emitter layer resistance as a measure of the amount of electrically active phosphorus atoms that have diffused in.

[0005] The phosphorus surface concentration can lie in the range of 10^{19} to more than 10^{21} atoms/cm^3, depending on the diffusion conditions and the type of doping agent, with the maximum concentration of electrically active phosphorus atoms as well as the solubility of phosphorus in silicon (approximately 5×10^{20} atoms/cm^3) being exceeded. The phosphorus is then present in inactive form and forms recombination centers for the charge carrier pairs generated (so-called “dead layer”).

[0006] The metal contacts on the front side are produced predominantly by means of thick-film silver pastes in the silk-screen printing process with subsequent sintering. On the one hand, a high phosphorus surface concentration is advantageous for the creation of a low-ohmic contact between the silver paste and the emitter; on the other hand, such a high surface concentration of the doping agent causes, as mentioned, a more enhanced recombination of the charge carrier pairs generated by light absorption.

[0007] An improvement of the emitter surface can be achieved by etching back of the highly doped layers near the surface. The surface recombination of the charge carriers generated is hereby reduced.

[0008] This is evident through improved spectral sensitivity and internal quantum efficiency in the short-wavelength region of the spectrum and positively influences above all the short-circuit current density as well as the open-circuit voltage of the solar cell.

[0009] According to the prior art, in a first chemical treatment step, the phosphosilicate glass formed from silicon oxide and from dopant oxides is removed in dilute hydrofluoric acid after diffusion during the production of solar cells with p-silicon-based wafers.

[0010] In a second treatment step, alkaline cleaning solutions, based on ammonia or alkyl ammonium hydroxides and hydrogen peroxide, are used. Solutions of this type were originally developed for semiconductor cleaning, known as “SC-1,” a part of the RCA cleaning sequence.

[0011] Standard RCA cleaning comprises treatment in the SC-1 solution, consisting of ammonia or ammonia derivatives and hydrogen peroxide, rinsing, and treatment with hydrogen peroxide in a dilute hydrochloric acid solution (known as “SC-2”). Ammonia and hydrochloric acid are generally employed in the concentration range of 3 to 10 weight percent; the hydrogen peroxide concentration generally is approximately 1 weight percent.

[0012] The temperatures employed are in the range of 60° C. to 85° C.; the contact times are approximately 10 minutes. Such conditions can be realized only in batch process units.

[0013] In widely employed continuous process units, solutions based on alkyl ammonium hydroxides and hydrogen peroxide are employed at temperatures of approximately 60° C. and contact times of approximately 60 s. For reasons of economic efficiency, markedly longer contact times cannot be implemented.

[0014] The change of the emitter layer resistance is a readily accessible measured parameter, by means of which the depth of the emitter etching back and the reduction in the surface concentration of the dopant can be measured approximately. Mass erosion due to the etching solution is very small (on the order of 1 mg for wafers that are 156×156 mm in size) and corresponds to the erosion of only a very thin emitter layer of less than 10 nm.

[0015] Emitters produced by standard methods have a layer resistance in the range of 50 to 70 ohm/sq after diffusion. The layer resistance is raised by 5 to 10 ohm/sq by treatment in dilute hydrofluoric acid and subsequent treatment in the RCA sequence, that is, 10 minutes in SC-1 solution, rinsing, and 10 minutes in SC-2 solution. The emitter etching back takes place predominantly in the alkaline SC-1 solution.

[0016] The layer resistance is increased by only approximately 1-2 ohm/sq by treatment in continuous process units at approximately 60° C. and a contact time of 60 s in a solution based on alkyl ammonium hydroxides and hydrogen peroxide.

[0017] Offered as an alternative cleaning and emitter etching solution is an acidic aqueous mixture made up of tetramethylammonium hydroxide (TMAH), acetic acid, surfactants, complex-forming agents, fluoride, and peroxide. This solution makes possible stronger etching back of the emitters even at lower temperatures, that is, at approximately 40° C.

[0018] The emitter can be strongly etched-back by using an acidic etching mixture consisting of nitric acid and hydrofluoric acid; that is, the increase of the emitter layer resistance is, for example, 20 ohm/sq and more at shorter contact time and lower temperature, such as, for example, 60 s at up to 15° C. The etching rate of this solution is too high for a controlled moderate etching back of a flat emitter. The remaining surface doping would be too small to form a low-ohmic contact with silk-screened silver paste. This solution can be used to produce a selective emitter. In this type of emitter, subregions beneath the metal contacts have a low layer resistance and a high surface concentration of the dopant as well as a high layer resistance between the metal contacts.

[0019] Described as another possibility for emitter batch etching is a repeated sequence consisting of chemical oxidation—for example, with nitric acid—and removal of the formed silicon oxide in dilute hydrofluoric acid. The etching back of the emitter in this way is very slow and requires several process solutions.

[0020] The drawback of the available alkaline solutions for emitter etching back is that the etching rate is too low. Long contact times and high temperatures are necessary for an expedient, uniform, and moderate etching back of the emitter and an increase in the layer resistance in the range between 5 and 15 ohm/sq.

[0021] Typical alkaline emitter etching solutions are based on ammonia or ammonia derivatives and hydrogen peroxide. By way of example, reference is made to the "SC1 solution" of the RCA cleaning developed for semiconductor manufacture (W. Kern, "The Evolution of Silicon Wafer Cleaning Technology" in J. Electrochem. Soc., Vol. 137, No. 6, June 1990, 1887-1891). Alkyl and hydroxyalkyl derivatives of ammonia offer the advantage of a lower vapor pressure and hence less of a problem with emissions in comparison to ammonia. Further components, such as complexing agents, surfactants, and stabilizers, can also be employed (see, for example, WO A 2006/039090).

[0022] The drawback of these solutions is the low etching back of the emitter surface layer within the contact time available in standard processes for solar cell manufacture, which usually is less than 1 min in a continuous process unit.

[0023] Described in EP A 1 843 389 is a sequence consisting of repeated chemical oxidation with subsequent dilute HF to remove the silicon oxide, so as to erode the uppermost highly doped emitter layers. Specified for chemical oxidation are: ozone, ozone/H_2O, $O_3/H_2O/HF$, H_2O_2, HNO_3, H_2SO_4, and NH_4OH at a temperature of between 20° C. and 90° C. This method is supposed to offer the advantage of a better degree of control of the emitter profile/phosphorus surface concentration created during diffusion with respect to oxidation. However, owing to chemical oxidation under the given conditions, an oxide layer with a thickness of only approximately 1 nm is produced. Several repetitions of the oxidation/HF sequence would be needed to erode the highly doped layer.

[0024] Described in EP A EP 0 731 495 as cleaning solutions for semiconductors in the framework of a modified RCA cleaning sequence are aqueous HF solutions containing ozone (and surfactant for improvement of the ozone solubility) or hydrogen peroxide.

[0025] An alternative possibility of avoiding the drawback of a high surface concentration of dopant is offered by the development of the selective emitter. Thus, the production of a selective emitter via etching back of an emitter, diffused by conventional processes, in the regions between the metal contacts may be inferred from WO A 2009/013307. The regions beneath the metal contacts are protected by an etching barrier introduced beforehand. In the first step, a mixture made up of nitric acid and hydrofluoric acid is used for etching back for controlled production of a porous silicon layer. The etching progress is readily evident, because the porous silicon appears in various colors depending on the layer thickness. In the second step, the porous silicon is subjected to wet-chemical oxidation. Specified as oxidants are HNO_3 and H_2SO_4. The removal of SiO_2 in dilute HF occurs subsequently.

[0026] A drawback of the mixed acid used is that it is difficult to control the formation of a homogenously porous Si layer by process engineering, so that—and as a consequence of inhomogeneous etching back—a strong scatter of the emitter layer resistance values over the wafer surface results.

[0027] The effect of alkaline emitter etching solutions based on TMAH and hydrogen peroxide may be inferred from the literature reference J. J. Tool et al. "Almost 1% Absolute Efficiency Increase in mc—Solar Cell Manufacturing with Simple Adjustment to the Processing Sequence," Proceedings 21st European Photovoltaic Solar Conference, Dresden (2006).

[0028] A cleaning sequence consisting of repeated oxidation with HNO_3 and oxide dissolution in HF may be taken from S. Keipert-Colberg et al., "Investigation and Development of Industrial Feasible Cleaning Sequences Prior to Silicon Nitride Deposition Enhancing Multicrystalline Silicon Solar Cell Efficiency," Proceedings 24th European Photovoltaic Solar Energy Conference, Hamburg (2009).

[0029] The present invention is based on the problem of further developing a method of the type mentioned in the beginning such that the drawbacks of prior art can be avoided. At the same time, homogenous etching back of the surface region of the emitter should be possible. Furthermore, it should be possible to employ process times and parameters that do not lead to a negative influence on the solar cell manufacturing process in a process line. It should also be possible to adjust precisely dopants, such as phosphorus surface concentrations. The blue sensitivity in solar cells should be improved.

[0030] In order to solve this problem, the invention provides essentially that an oxidant-free alkaline etching solution, containing at least one organic moderator, is used for isotropic etching back of the emitter in its surface region, which has a dopant concentration of at least 10^{18} atoms/cm^3, particularly at least 10^{19} atoms/cm^3. It is provided, in particular, that the etching solution used is one in which the alkaline component lies in the concentration range between 1 g/L (0.1 wt %) and 50 g/L (5 wt %). In particular, it is provided that the concentration range of the alkaline component lies between 2 g/L (0.2 wt %) and 15 g/L (1.5 wt %). Furthermore, the etching solution used should be one whose organic moderator lies in the concentration range between 0.1 g/L (0.01 wt %) and 5 g/L (0.5 wt %), in particular in the range between 0.2 g/L (0.02 wt %) and 1 g/L (0.1 wt %). Furthermore, it is provided, in particular, that the contact time between etching solution and the surface region is between 10 sec and 80 sec, preferably between 15 sec and 60 sec, with the temperature of the etching solution preferably being in the range between 35° C. and 65° C., particularly between 45° C. and 60° C.

[0031] On the basis of the teaching of the invention, the surface region of the emitter, which exhibits planar homogeneous doping, that is, lateral homogeneous doping, with at least a dopant concentration of greater than 10^{18} atoms/cm^3, is isotropically etched-back, with the topography of the previously textured surface being maintained. An emitter surface layer of constant thickness is consequently eroded. It is provided, in particular, that, through the choice of contact time and temperature as well as the concentration ranges of the alkaline component and of the organic moderator, less than 10 nm is eroded, in particular between 3 nm and 7 nm, preferably in the range of about 5 nm.

[0032] The teaching of the invention avoids anisotropic etching without alteration of the topography of the surface, so that even fragile structures projecting from the surface are retained.

[0033] Proposed in accordance with the invention is a method for a microscopically homogeneous, wet-chemical, isotropic depth etching of a highly doped emitter zone near the surface, with the greatest degree of retention of the topographic details of the surface having a dopant concentration of more than 10^{18} atoms/cm^3 and a preferred back-etching depth of between 3 nm and 7 nm, in particular <5 nm, by using an oxidant-free alkaline etching solution containing at least one organic moderator as etching solution.

[0034] Although the use of alkaline etching solutions containing organic moderators is known, they are not known for isotropic etching back of a highly doped surface region of an emitter of a silicon-based crystalline solar cell.

[0035] Thus, a texturing and cleaning medium for surface treatment of wafers may be inferred from DE A 10 2007 058 829. Proposed is an anisotropic etching for creation of surface roughness, so as to minimize light reflections. Because of the anisotropy, the alkaline solutions used are suitable only for texturing of monocrystalline silicon, with pyramids being formed. Coming into consideration as etching medium are KOH, NaOH, THAH, or other inorganic etching media.

[0036] Provided as additives are aliphatic and aromatic carboxylic acids, amino carboxylic acids, polyalcohols, EDTA, polyethylene sorbitan monolaurate, and alkly-substituted pyrocatechol. The concentration of the etching medium lies between 4 and 15 wt % and that of the additives between 1 and 20 wt %. Provided as contact times are 10-30 min at a temperature of greater than 80° C. The silicon layer that is etched off lies in the range of between 5 and 10 μm. Use for etching back a highly doped emitter surface region is not possible with a respective etching solution, because the emitter layer would be totally destroyed in the case of conventional emitter thicknesses in the range of 350 nm.

[0037] The subject of DE A 10 2008 052 660 is a method for manufacturing a solar cell with two-stage doping. A selective emitter is supposed to be produced by means of an inorganic mask. The mask is produced by application of a paste, which contains SiO_2 glass, and subsequent fusion. HF—HNO_3 is used for etching back. In this process, the mask is partially or completely co-etched off. Employed for removal of the porous silicon resulting from the etching is an alkaline etching solution. The function of the alkaline etching solution involves selectively etching off the porous silicon layer that was created beforehand in an upstream acidic etching step. An isotropic etching back in the range of 5 nm cannot be controlled using the respective measures.

[0038] Carried out in accordance with the invention, by contrast, is a one-step, chemically simple process, which, in comparison to the technically difficult process that, owing to the toxicity of hydrofluoric acid, is also risky, is quite suitable economically.

[0039] An anisotropic etching by means of KOH with isopropanol, for example, is described in GB A 2 209 245 for the creation of a three-dimensional structure. In this process, more highly doped regions are selectively removed. Described is a multi-stage method for producing lateral etched steps in the surface, with the creation of a highly boron-doped surface that is resistant to the anisotropically acting etching medium.

[0040] A substrate that is 40 nm thick is thinned to 10 nm according to US A 2004/0259324. Used as etching medium is an alkaline etching medium, which contains quaternary ammonium hydroxides, substituted amines, particularly TMAH in a concentration of between 10 wt % and 45 wt %. The etching rate at 25° C. amounts to 7.5 nm/min. Provided as possible further additives in the etching solution are anionic, cationic, and neutral surfactants, oxidants in the form of peroxide or persulfate, or, alternatively, reductants. Acids such as silicic acid can also be employed to change the pH. The described method is aimed at substantial thinning of the substrate made of silicon, with the attainment back-etching depths that, solely on account of the etching rate, do not lead to reproducibly adjustable back-etching depths for highly doped emitters.

[0041] Etching solutions for undoped silicon, highly doped silicon, and silicon nitride are also known from US A 2005/0065050. The etching solution is supposed to enable the highest possible etching selectivity, that is, different etching rates for the respective substrates, to be achieved. Coming into consideration as etching medium are, for example, KOH or TMAH. Possible additives have the properties of being water soluble, non-volatile, non-flammable, with preferably ethylene glycol being specified. The etching method aims at the manifestation of a high selectivity of the etching rate of various dopant concentrations in the silicon or at the boundary surfaces to adjacent layers, such as SiH or SiOx.

[0042] A selective dissolution of any unevenness in a thin-layer film is the subject of US A 2010/0126961. The etching solution consists of a strong base, such as TMAH, NaOH, or KOH, an etching moderator, an oxidant, such as a persulfates, and a wetting agent. The contact time between the etching solution and the polysilicon thin-layer film that is being planarized lies between 0.5 min and 10 min at a temperature between 40° C. and 80° C. Projections on a size order of between 80 nm and 100 nm are supposed to be etched. Corresponding etching solutions are not suitable for controlled used on highly doped surface regions of an emitter, particularly for a back-etching depth of <5 nm.

[0043] A selective etching of non-doped regions in silicon is described in U.S. Pat. No. 5,431,777. Coming into consideration as etching medium are KOH, NaOH, and TMAH in a concentration range of approximately 8 wt %. As additives, it is possible also to use aromatic alcohols and ethers, including substituted ones, Novolacs, and polyvinyl alcohol. The etching rate ranges from a few nanometers to a few micrometers per minute, with a temperature range of between 45° C. and 104° C. be chosen.

[0044] EP A 2 302 701 relates to the texturing of a semiconductor substrate. Coming into consideration as etching medium are hydroxides and alkanol amines. The concentration range for use of KOH is given as 6 wt % by way of example. Coming into consideration as additives are alkoxylated glycols or glycol alkyl ethers, such as triethylene glycol and diethylene glycol monomethyl ether. Additionally provided are chlorides and silicates. The etching erosion approaches 10 μm at temperatures of between 80° C. and 100° C. The described mixtures are utilized for anisotropic texturing of a Si surface.

[0045] The subject of the invention is an alkaline etching solution containing at least one organic etching moderator. This solution makes possible an optimal etching back of the emitter within short contact times, because the etching rate for silicon is higher than that of alkaline solutions that contain hydrogen peroxide as etching-moderating component.

[0046] Another advantage of the solution according to the invention is that porous silicon, which can form in preceding process steps, is removed.

[0047] Surface-active substances (surfactants) can be employed as organic moderators that inhibit the etching attack of the alkaline solutions. Because surfactant molecules contain a hydrophobic group and a hydrophilic group, both H-terminated (hydrophobic) and oxidized (hydrophilic) substrate surfaces are protected.

[0048] The advantage of organic moderators over hydrogen peroxide is that the silicon surface is not completely "blocked." Moderate and uniform silicon dissolution is still not yet possible. Hydrogen peroxide results in oxidation of the silicon surface; the etching rate of silicon oxide in an alkaline solution is extremely low. Even at very low concentrations, hydrogen peroxide is effective above 0.1 wt %. Smaller concentrations do not interfere and can also be present in the etching solutions according to the invention. Hence, it is insofar possible to speak of an oxidant-free aqueous etching solution.

[0049] It has been found that many surface-active substances produce the desired moderating effect on the etching operation. Differences in the adsorption strength of surfactants on the silicon surface and hence in their ability to moderate the etching attack of the alkaline solution can be compensated for by adjusting the surfactant and alkaline concentration as well as by adjusting the etching parameters temperature and time to the desired etching rate or else to the desired increase in the emitter layer resistance.

[0050] The solution according to the invention contains an alkaline component and at least one organic etching moderator. Complexing agents and buffering substances can be employed as further constituents.

[0051] Used as alkaline component is at least one substance from the group of LiOH, NaOH, KOH, ammonium hydroxide, quaternary ammonium hydroxides, organic bases, and organic amines.

[0052] Quaternary ammonium hydroxides comprise tetraalkyl ammonium hydroxides and substituted tetraalkyl ammonium hydroxides containing hydroxyl- and alkoxy-substituted alkyl groups, such as, for example, tetraalkyl ammonium hydroxide, trimethyl-2-hydroxyethylammonium hydroxide (choline), and triethyl(ethoxypropyl)ammonium hydroxide.

[0053] Examples of organic bases are pyrimidine and guanidine.

[0054] Organic amines comprise alkyl amines, polyalkylene amines, alkanolamines, cyclic N-substituted amines, and derivatives containing substituted alkyl groups.

[0055] Examples of alkyl amines are mono-, di-, and triethylamine and dodecyldimethylamine. An example of polyalkylene amines is diethylenetriamine. Examples of alkanolamines are mono-, di-, and triethanolamine and 2-(2-aminoethoxy)ethanol.

[0056] Examples of cyclic N-substituted amines are N-methylpyrrolidine, N-methylpiperidine, and N-ethylpyrrolidone.

[0057] The following substances can be employed as etching moderators.

[0058] anionic surfactants, such as sulfuric acid alkyl esters and the salts thereof, alkyl carboxylic acids and the salts thereof, alkyl and alkyl benzene sulfonic acids and the salts thereof, mono- and diesters of orthophosphates, fluorinated carboxylic acids, and fluorinated sulfonic acids,

[0059] nonionic surfactants, such as polyalkylene glycol ethers (for example, fatty alcohol ethoxylates, fatty alcohol propoxylates), alkyl polyglucosides, saccharose esters, sorbitan fatty acid esters, N-methylglucamides, alkyl phenol ethoxylates and alkyl phenol propoxylates, alkanol amides, alkyne diols, substituted alkynols, ethoxylated alkyne diols, and fluorinated alkyl alkoxylates,

[0060] amphoteric surfactants, such as alkyl betaines, amidoalkyl betaines, alkyl sulfobetaines, amidoalkyl sulfobetaines, alkyl amino oxides, alkyl amidoalkyl amino oxides, and fluorinated amphoteric alkyl compounds,

[0061] cationic surfactants, such as amine ethoxylates, dialkyl dimethyl ammonium salts, and alkyl benzyldimethyl ammonium salts.

[0062] Examples of anionic surfactants are: sodium dodecyl hydrogen sulfate, sulfosuccinic acid dihexyl ester, sodium dodecylbenenesulfonate, ammonium lauryl sulfate, 2-ethylhexanol phosphoric acid ester, and perfluorooctanesulfonate.

[0063] Examples of nonionic surfactants are: tetraethylene glycol octyl ether, lauryl myristyl polyglycol ether, octylphenol ethoxylate, saccharose stearic acid ester, and 3,5-dimethylhexyn-3-ol.

[0064] Examples of amphoteric surfactants are: cocoamidopropyl betaine, dodecyldimethyl-amino oxide, octylimino dipropionate, and N-dodecyl-N,N-dimethylammonium propanesulfonate.

[0065] Examples of cationic surfactants are: oleyl bis(2-hydroxyethyl)methylammonium chloride, dioctyldimethylammonium chloride, and cocobenzyldimethylammonium chloride.

[0066] The emitter solution can additionally contain:

[0067] complexing agents for silicic acid (reaction product), such as, for example, o-dihydroxybenzene and other hydroxyphenols as well as aromatic ethers,

[0068] complex-forming agents or chelating agents for metal cations: amines such as EDTA, DTPA, di- and tricarboxylic acids, hydroxycarboxylic acids (for example, citric acid, tartaric acid), polyalcohols, such as, for example, glycerin, sorbitol, and other sugars and sugar alcohols, phosphonic acids, and polyphosphates,

[0069] buffering substances, such as ammonium acetate and potassium hydrogen phthalate,

[0070] peroxides, such as hydrogen peroxide in very low concentrations (<0.1 wt %).

[0071] In addition, the invention is characterized by the use of one of the previously described etching solutions for etching back of the emitter, with a metal layer being deposited at least selectively onto the surface of the crystalline solar cell by chemical deposition or electrodeposition of a nickel/silver or nickel/copper layer or by physical vapor deposition methods after etching back of the emitter. When a vapor deposition method is used, a titanium/palladium/silver layer, in particular, is deposited.

[0072] The field of application of the invention is the manufacture of solar cells made of silicon. Therefore, the invention is characterized by a solar cell, the emitter of which is etched-back by using measures that have been previously described.

[0073] The invention will be discussed below on the basis of examples, from which ensue further features, in themselves and/or in combination.

EXAMPLE 1

[0074] The etching effect of a hydrogen peroxide-containing alkaline solution on the emitter of a solar cell was compared with the etching effect of a surfactant-containing solution. The hydrogen peroxide-containing solution contained 1 to 6 weight percent caustic soda and approximately 2 weight percent hydrogen peroxide. The temperature was in the range of 49° C. to 55° C. The surfactant-containing solution contained 1.2 weight percent NaOH and 0.1 wt % sodium dodecylbenzenesulfonate. The temperature of the solution was constant at 53° C.

[0075] Multicrystalline wafers, after diffusion and after chemical edge isolation, including dissolution of phosphosilicate glass in dilute hydrofluoric acid, were etched in the alkaline solutions. The contact times and the resulting increase in the emitter layer resistance are compiled in Table 1 and 2.

Emitter Layer Resistance

[0076]

TABLE 1

Increase in the emitter layer resistance by treatment in hydrogen peroxide-containing solution.

Solution	Contact time seconds	Before etching ohm/sq	After etching ohm/sq	Delta ohm/sq
NaOH 1 wt %, H_2O_2 2 wt %	60	48.1	48.7	0.6
	300	49.3	50.5	1.2
NaOH 3 wt %, H_2O_2 2 wt %	30	49.6	50.2	0.6
	300	48.8	51.4	2.6

Emitter Layer Resistance

[0077]

TABLE 2

Increase in the emitter layer resistance by treatment in surfactant-containing solution.

Solution	Contact time seconds	Before etching ohm/sq	After etching ohm/sq	Delta ohm/sq
NaOH 1.2 wt %, sodium dodecylbenzenesulfonate 0.1 wt %	25	54.0	58.9	4.9
	50	55.3	68.1	12.8
	75	55.9	78.6	22.7

[0078] It can be seen from the values that the etching rate of the surfactant-containing solution is markedly higher than that of the hydrogen peroxide-containing solution.

EXAMPLE 2

[0079] Multicrystalline wafers, after diffusion, were etched in a hydrogen peroxide-containing or in a surfactant-containing solution after chemical edge isolation, including dissolution of phosphosilicate glass in hydrofluoric acid. The wafers were then coated with a silicon nitride antireflection layer in standard production processes and metallicized in the silk-screen printing process. The electrical values of the cells as well as the emitter layer resistance directly before a nitride coating are presented in Table 3.

TABLE 3

Electrical values after emitter etching back in a hydrogen peroxide-containing or surfactant-containing solution.

Emitter etching solution	Voc [mV]	Jsc [mA/ cm^2]	FF	Eta [%]	R_{sheet} Ω/□
NaOH, 1.2 wt %, hydrogen peroxide 0.3 wt % (20° C., contact time 40 s)	0.609	34.07	0.772	16.02	64.0
NaOH, 1.2 wt %, sodium dodecylbenzenesulfonate 0.1 wt % (50° C., contact time 25 s)	0.611	34.27	0.771	16.14	67.3

[0080] After a stronger etching back of the emitter, that is, at higher layer resistance, higher short-circuit current densities (Jsc) and higher open-circuit voltages (Voc) are observed, resulting in a higher efficiency of the solar cells.

EXAMPLE 3

[0081] The etching effect of the solution according to the invention from Example 1 and 2 was compared with the etching effect of a cleaning solution consisting of 1 weight percent tetramethylammonium hydroxide (TMAH) and 1 weight percent hydrogen peroxide.

[0082] Used were multicrystalline wafers after diffusion and chemical edge isolation, including dissolution of phosphosilicate glass in dilute hydrofluoric acid. After treatment in the emitter etching solutions was finished, further standard production processes were carried out.

[0083] The electrical values and the increase in the emitter layer resistance are compiled in Table 4.

TABLE 4

Electrical values after emitter etching back in a solution according to the invention and in an aqueous solution containing TMAH and hydrogen peroxide.

Emitter etching solution	Voc [mV]	Jsc [mA/ cm^2]	FF	Eta [%]	Delta R_{sheet} Ω/□
NaOH, 1.2 wt %, sodium dodecylbenzenesulfonate 0.1 wt % (50° C., contact time 25 s)	0.603	34.24	0.768	15.84	5.0
Tetramethylammonium hydroxide 1.0 wt %, hydrogen peroxide 1.0 wt % (60° C., contact time 60 s)	0.601	34.03	0.769	15.77	1.5

EXAMPLE 4

[0084] Multicrystalline wafers, after diffusion, with an emitter layer resistance of 48 ohm/sq, were treated in a vertical laboratory unit initially in dilute hydrofluoric acid for 2 minutes, rinsed, and subsequently etched in a solution of the following composition for 2 minutes at 50° C.

[0085] KOH, 1.5 wt %

[0086] ammonium lauryl sulfate, 0.5 wt %

[0087] 1,2-dihydroxybenzene (pyrocatechol), 0.1 wt %

[0088] The measured layer resistance after treatment in the etching solution was on average 53 ohm/sq.

EXAMPLE 5

[0089] In the same arrangement as in Example 2, a solution of the following composition was used.

[0090] tetramethylammonium hydroxide, 1 wt %

[0091] ammonium lauryl sulfate, 0.1 wt %

[0092] diethlyenetriaminepentaacetic acid, 0.05 wt %

[0093] Monocrystalline wafers, after diffusion, with an emitter layer thickness of 52 ohm/sq, were treated in dilute HF for 2 minutes, rinsed, and etched at 60° C. for 1 minute in the solution according to the invention. The measured layer resistance was on average 58 ohm/sq. The increase in layer resistance was thus 6 ohm/sq.

EXAMPLE 6

[0094] An aqueous emitter etching solution with the following composition was employed:

[0095] diethylenetriamine, 3.5 wt %

[0096] dodecyldimethlyamine oxide, 0.1 wt %

[0097] ammonium chloride, 0.5 wt %

[0098] hydrogen peroxide, 0.06 wt %

[0099] Used were multicrystalline wafers after inline diffusion. After removal of phosphosilicate glass and after chemical edge isolation in a horizontal unit, the emitter layer resistance was 53 ohm/sq.

[0100] After 1 minute of treatment time in a vertical laboratory unit at 50° C. in the solution according to the invention, the layer resistance was on average 56 ohm/sq.

1-19. (canceled)

20. A method for the wet-chemical etching of a surface region of a solar cell emitter in an alkaline etching solution, comprising:

isotropic etching back the surface region using an oxidant-free alkaline etching solution comprising at least one organic moderator, the surface region has a dopant concentration of at least 10^{18} atoms/cm^3.

21. The method according to claim **20**, wherein the oxidant-free alkaline etching solution has an alkaline component in a concentration range between 1 g/L and 50 g/L.

22. The method according to claim **20**, wherein the oxidant-free alkaline etching solution has a concentration range of the at least one organic moderator between 0.1 g/L and 5 g/L.

23. The method according to claim **20**, wherein the step of isotropic etching back comprises contacting the surface region with the oxidant-free alkaline etching solution for a time between greater than or equal to 10 second and less than or equal to 180 seconds.

24. The method according to claim **23**, wherein the time is between greater than or equal to 15 seconds and less than or equal to 16 seconds.

25. The method according to claim **20**, further comprising adjusting the oxidant-free alkaline etching solution to a temperature of between less than or equal to 35° C. and greater than or equal to 65° C. during the etching back.

26. The method according to claim **21**, wherein the alkaline component has at least one component selected from the group consisting of LiOH, NaOH, KOH, ammonium hydroxide, quaternary ammonium hydroxides, tetraalkyl ammonium hydroxide, organic bases, and organic amines.

27. The method according to claim **20**, wherein the organic moderator comprises at least one component selected from the group consisting of sulfuric acid alkyl esters and the salts thereof, alkyl carboxylic acids and the salts thereof, alkyl and alkyl benzene sulfonic acids and the salts thereof, mono- and diesters of orthophosphates, fluorinated carboxylic acids, fluorinated sulfonic acids, polyalkylene glycol ethers, such as fatty alcohol ethoxylates or fatty alcohol propoxylates, alkyl polyglucosides, saccharose esters, sorbitan fatty acid esters, N-methylglucamides, alkyl phenol ethoxylates, alkyl phenol propoxylates, alkanol amides, alkyne diols, substituted alkynols, ethoxylated alkyne diols, fluorinated alkyl alkoxylates, alkyl betaines, amidoalkyl betaines, alkyl sulfobetaines, amidoalkyl sulfobetaines, alkyl amino oxides, alkyl amidoalkyl amino oxides, fluorinated amphoteric alkyl compounds, alkyl amine ethoxylates, dialkyl dimethyl ammonium salts, and alkyl benzyldimethyl ammonium salts.

28. The method according to claim **20**, wherein the oxidant-free alkaline etching solution further comprises at least one component selected from the group consisting of complexing agents, complexing agents for silicic acid, complexing agents for metal cations, chelating agents for metal cations, and buffering substances.

29. The method according to claim **20**, wherein the at least one organic moderator is a surface-active substance or surfactant.

30. The method according to claim **20**, wherein the at least one organic moderator comprises at least one component selected from the group consisting of sodium dodecylbenzenesulfonate, saccharose stearic acid ester, dodecyldimethylamino oxide, and dioctyldimethylammonium chloride.

31. The method according to claim **20**, wherein the step of isotropic etching back the surface region comprises etching back the surface region to a thickness between 0 and less than or equal to 10 nm.

32. The method according to claim **28**, wherein the complexing agent is selected from the group consisting of hydroxyphenols, amines, hydroxycarboxylic acids, polyalcohols, phosphonic acids, and polyphosphates.

33. The method according to claim **20**, wherein the step of isotropic etching back the surface region comprises employing the oxidant-free alkaline etching solution in batch processing unit or continuous process unit.

34. The method according claim **20**, wherein the surface region comprises, as a dopant, a material selected from the group consisting of phosphorus, arsenic, boron, gallium, and aluminum.

35. A crystalline solar cell with a solar cell emitter that is etched-back according to the method of claim **20**.

36. A method for the wet-chemical etching of a surface region of a solar cell emitter in an alkaline etching solution, comprising:

isotropic etching back the surface region using an oxidant-free alkaline etching solution containing at least one organic moderator, the surface region having a dopant concentration of at least 10^{18} atoms/cm^3,

wherein the oxidant-free alkaline etching has an alkaline component with a concentration range between 1 g/L and 50 g/L and the organic moderator has a concentration range that lies between 0.1 g/L and 5 g/L,

wherein the step of isotropic etching back comprises contacting the surface region with the oxidant-free alkaline etching solution for a time between greater than or equal to 10 second and less than or equal to 180 seconds; and

adjusting the oxidant-free alkaline etching solution to a temperature of between less than or equal to 35° C. and greater than or equal to 65° C. during the etching back.

37. The method according claim **36**, further comprising, after the step of isotropic etching back, applying a metal layer at least selectively onto the surface region by a method selected from the group consisting of chemical deposition, electrodeposition, and physical vapor deposition.

38. The method according claim **37**, wherein the metal layer comprises a layer selected from the group consisting of nickel/silver layer, a nickel/copper layer, and a titanium/palladium/silver layer.

39. A crystalline solar cell with a solar cell emitter that is etched-back according to the method of claim **36**.

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