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(54) Title: AGENT FOR INCREASING ETCHING RATES

(57) Abstract: The present invention relates to an etching composition for the etching of surfaces consisting of Si, SiO₂, SiN_x or transparent conductive oxides (TCO), comprising at least one aqueous phase and at least an agent for increasing etch rates, and to the use of said composition in production processes in electronic industry.



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Agent for Increasing Etching Rates

5 The present invention relates to an etching composition for the etching of surfaces consisting of Si, SiO₂, SiN_x or transparent conductive oxides (TCO), comprising at least one aqueous phase and at least an agent for increasing etch rates, and to the use of said composition in production processes in electronic industry.

10 State of the art

The production of simple solar cells or solar cells which are currently represented with the greatest market share in the market comprises the essential production steps outlined below:

15 1. Saw-damage etching and texture

20 A silicon wafer (monocrystalline, multi-crystalline or quasi-monocrystalline, base doping p or n type) is freed from adherent saw damage by means of etching methods and "simultaneously" textured, generally in the same etching bath. Texturing is in this case taken to mean the creation of a preferentially aligned surface (nature) as a consequence of the etching step or simply the intentional, but not particularly aligned roughening of the wafer surface. As a consequence of the texturing, the surface of the wafer now acts as a
25 diffuse reflector and thus reduces the directed reflection, which is dependent on the wavelength and on the angle of incidence, ultimately resulting in an increase in the absorbed proportion of the light incident on the surface and thus an increase in the conversion efficiency of the same solar cell.

30 The above-mentioned etch solutions for the treatment of the silicon wafers typically consist, in the case of monocrystalline wafers, of dilute potassium hydroxide solution to which isopropyl alcohol has been added as solvent. Other alcohols having a higher vapour pressure or a higher boiling point than isopropyl alcohol may also be added instead if this enables the desired
35 etching result to be achieved. The desired etching result obtained is typically a morphology which is characterised by pyramids having a square base

which are randomly arranged, or rather etched out of the original surface. The density, the height and thus the base area of the pyramids can be partly influenced by a suitable choice of the above-mentioned components of the etch solution, the etching temperature and the residence time of the wafers in the etching tank. The texturing of the monocrystalline wafers is typically carried out in the temperature range from 70 – < 90°C, where etching removal rates of up to 10 µm per wafer side can be achieved.

In the case of multicrystalline silicon wafers, the etch solution can consist of potassium hydroxide solution having a moderate concentration (10 – 15%). However, this etching technique is hardly still used in industrial practice. More frequently, an etch solution consisting of nitric acid, hydrofluoric acid and water is used. This etch solution can be modified by various additives, such as, for example, sulfuric acid, phosphoric acid, acetic acid, N-methylpyrrolidone and also surfactants, enabling, inter alia, wetting properties of the etch solution and also its etching rate to be specifically influenced. These acidic etch mixtures produce a morphology of nested etching trenches on the surface. The etching is typically carried out at temperatures in the range between 4°C and < 10°C, and the etching removal rate here is generally 4 µm to 6 µm.

Immediately after the texturing, the silicon wafers are cleaned intensively with water and treated with dilute hydrofluoric acid in order to remove the chemical oxide layer formed as a consequence of the preceding treatment steps and contaminants absorbed and adsorbed therein and also thereon, in preparation for the subsequent high-temperature treatment.

2. Diffusion and doping

The wafers etched and cleaned in the preceding step (in this case p-type base doping) are treated with vapour consisting of phosphorus oxide at elevated temperatures, typically between 750°C and < 1000°C. During this operation, the wafers are exposed to a controlled atmosphere consisting of dried nitrogen, dried oxygen and phosphoryl chloride in a quartz tube in a tubular furnace. To this end, the wafers are introduced into the quartz tube at temperatures between 600 and 700°C. The gas mixture is transported

through the quartz tube. During the transport of the gas mixture through the strongly warmed tube, the phosphoryl chloride decomposes to give a vapour consisting of phosphorus oxide (for example P_2O_5) and chlorine gas. The phosphorus oxide vapour precipitates, inter alia, on the wafer surfaces (coating). At the same time, the silicon surface is oxidised at these temperatures with formation of a thin oxide layer. The precipitated phosphorus oxide is embedded in this layer, causing mixed oxide of silicon dioxide and phosphorus oxide to form on the wafer surface. This mixed oxide is known as phosphosilicate glass (PSG). This PSG has different softening points and different diffusion constants with respect to the phosphorus oxide depending on the concentration of the phosphorus oxide present. The mixed oxide serves as diffusion source for the silicon wafer, where the phosphorus oxide diffuses in the course of the diffusion in the direction of the interface between PSG and silicon wafer, where it is reduced to phosphorus by reaction with the silicon on the wafer surface (silicothermally). The phosphorus formed in this way has a solubility in silicon, which is orders of magnitude higher than in the glass matrix from which it has been formed and thus preferentially dissolves in the silicon owing to the very high segregation coefficient. After dissolution, the phosphorus diffuses in the silicon along the concentration gradient into the volume of the silicon. In this diffusion process, concentration gradients in the order of 10^5 form between typical surface concentrations of 10^{21} atoms/cm² and the base doping in the region of 10^{16} atoms/cm². The typical diffusion depth is 250 to 500 nm and is dependent on the diffusion temperature selected (for example 880°C) and the total exposure duration (heating & coating phase & drive-in phase & cooling) of the wafers in the strongly warmed atmosphere. During the coating phase, a PSG layer forms which typically has a layer thickness of 40 to 60 nm. The coating of the wafers with the PSG, during which diffusion into the volume of the silicon also already takes place, is followed by the drive-in phase. This can be decoupled from the coating phase, but is in practice generally coupled directly to the coating in terms of time and is therefore usually also carried out at the same temperature. The composition of the gas mixture here is adapted in such a way that the further supply of phosphoryl chloride is suppressed. During the injection, the surface of the silicon is oxidised further by the oxygen present in the gas mixture, causing a phosphorus oxide-depleted silicon dioxide layer which likewise comprises phosphorus oxide to be gener-

ated between the actual doping source, the highly phosphorus oxide-enriched PSG, and the silicon wafer. The growth of this layer is very much faster in relation to the mass flow of the dopant from the source (PSG), since the oxide growth is accelerated by the high surface doping of the wafer itself (acceleration by one to two orders of magnitude). This enables depletion or separation of the doping source to be achieved in a certain manner, permeation of which with phosphorus oxide diffusing on is influenced by the material flow, which is dependent on the temperature and thus the diffusion coefficient. In this way, the doping of the silicon can be controlled in certain limits. A typical diffusion duration consisting of coating phase and injection phase is, for example, 25 minutes. After this treatment, the tubular furnace is allowed to cool down, and the wafers can be removed from the process tube at temperatures between 600°C and 800°C.

In the case of boron doping of the wafers in the form of an n-type base doping, a different method is carried out, which will not be explained separately here. The doping in these cases is carried out, for example, with boron trichloride or boron tribromide. Depending on the choice of the composition of the gas atmosphere employed for the doping, the formation of a so-called boron skin on the wafers may be observed. This boron skin is dependent on various influencing factors: crucially the doping atmosphere, the temperature, the doping duration, the source concentration and the coupled (or linear-combined) parameters mentioned above.

In such diffusion processes, it goes without saying that the wafers used cannot contain any regions of preferred diffusion and doping (apart from those which are formed by inhomogeneous gas flows and resultant gas pockets of inhomogeneous composition) if the substrates have not previously been subjected to a corresponding pretreatment (for example structuring thereof with diffusion-inhibiting and/or –suppressing layers and materials).

For completeness, it should also be pointed out here that there are also further diffusion and doping technologies which have become established to different extents in the production of crystalline solar cells based on silicon. Thus, mention may be made of

- ion implantation,

- doping promoted via the gas-phase deposition of mixed oxides, such as, for example, those of PSG and BSG (borosilicate glass), by means of APCVD, PECVD, MOCVD and LPCVD processes,
- 5 - (co)sputtering of mixed oxides and/or ceramic materials and hard materials (for example boron nitride),
- gas-phase deposition of the last two,
- purely thermal gas-phase deposition starting from solid dopant sources (for example boron oxide and boron nitride) and
- 10 - liquid-phase deposition of doping liquids (inks) and pastes.

10 The latter are frequently used in so-called inline doping, in which the corresponding pastes and inks are applied by means of suitable methods to the wafer side to be doped. After or also even during the application, the solvents present in the compositions employed for the doping are removed by

15 temperature and/or vacuum treatment. This leaves the actual dopant on the wafer surface. Liquid doping sources which can be employed are, for example, dilute solutions of phosphoric or boric acid, and also sol-gel-based systems or also solutions of polymeric borazil compounds. Corresponding doping pastes are characterised virtually exclusively by the use of additional

20 thickening polymers, and comprise dopants in suitable form. The evaporation of the solvents from the above-mentioned doping media is usually followed by treatment at high temperature, during which undesired and interfering additives, but ones which are necessary for the formulation, are either "burnt" and/or pyrolysed. The removal of solvents and the burning-out may,

25 but do not have to, take place simultaneously. The coated substrates subsequently usually pass through a belt furnace at temperatures between 800°C and 1000°C, where the temperatures may be slightly increased compared with gas-phase diffusion in the tubular furnace in order to shorten the passage time. The gas atmosphere prevailing in the belt furnace may differ

30 in accordance with the requirements of the doping and may consist of dry nitrogen, dry air, a mixture of dry oxygen and dry nitrogen and/or, depending on the design of the furnace to be passed through, zones of one or other of the above-mentioned gas atmospheres. Further gas mixtures are conceivable, but currently do not have major importance industrially. A

35 characteristic of inline diffusion is that the coating and drive-in of the dopant can take place in principle decoupled from one another.

3. Removal of the dopant source and optional edge insulation

The wafers present after the doping are coated on both sides with more or less glass on both sides of the surface. More or less in this case refers to modifications, which can be applied during the doping process: double-sided diffusion vs. quasi-single-sided diffusion promoted by back-to-back arrangement of two wafers in one location of the process boats used. The latter variant enables predominantly single-sided doping, but does not completely suppress diffusion on the back. In both cases, it is currently state of the art to remove the glasses present after the doping from the surfaces by means of etching in dilute hydrofluoric acid. To this end, the wafers are firstly re-loaded in batches into wet-process boats and with their aid dipped into a solution of dilute hydrofluoric acid, typically 2% to 5%, and left therein until either the surface has been completely freed from the glasses, or the process cycle duration, which represents a sum parameter of the requisite etching duration and the process automation by machine, has expired. The complete removal of the glasses can be established, for example, from the complete dewetting of the silicon wafer surface by the dilute aqueous hydrofluoric acid solution. The complete removal of a PSG is achieved within 210 seconds at room temperature under these process conditions, for example using 2% hydrofluoric acid solution. The etching of corresponding BSGs is slower and requires longer process times and possibly also higher concentrations of the hydrofluoric acid used. After the etching, the wafers are rinsed with water.

On the other hand, the etching of the glasses on the wafer surfaces can also be carried out in a horizontally operating process, in which the wafers are introduced in a constant flow into an etcher in which the wafers pass horizontally through the corresponding process tanks (inline machine). In this case, the wafers are conveyed on rollers either through the process tanks and the etch solutions present therein, or the etch media are transported onto the wafer surfaces by means of roller application. The typical residence time of the wafers during etching of the PSG is about 90 seconds, and the hydrofluoric acid used is somewhat higher concentrated than in the case of the batch process in order to compensate for the shorter residence time as a result of an increased etching rate. The concentration of the hydrofluoric acid

is typically 5%. Additionally the tank temperature may optionally be slightly increased compared with room temperature ($> 25^{\circ}\text{C} < 50^{\circ}\text{C}$).

5 In the process outlined last, it has become established to carry out the so-called edge insulation sequentially at the same time, giving rise to a slightly modified process flow: edge insulation $\rightarrow$ glass etching. The edge insulation is a process-engineering necessity, which arises from the system-inherent characteristic of double-sided diffusion, also in the case of intentional single-sided back-to-back diffusion. A large-area parasitic p-n junction is present on
10 the (later) back of the solar cell, which is, for process-engineering reasons, removed partially, but not completely, during the later processing. As a consequence of this, the front and back of the solar cell are short-circuited via a parasitic and residual p-n junction (tunnel contact), which reduces the conversion efficiency of the later solar cell. For removal of this junction, the
15 wafers are passed on one side over an etch solution consisting of nitric acid and hydrofluoric acid. The etch solution may comprise, for example, sulfuric acid or phosphoric acid as secondary constituents. Alternatively, the etch solution is transported (conveyed) via rollers onto the back of the wafer. The etch removal rate typically achieved in this process is about $1\text{ }\mu\text{m}$ of silicon
20 (including the glass layer present on the surface to be treated) at temperatures between 4°C and 8°C . In this process, the glass layer still present on the opposite side of the wafer serves as mask, which provides a certain protection against etch encroachment on this side. This glass layer is subsequently removed with the aid of the glass etching already described.

25 In addition, the edge insulation can also be carried out with the aid of plasma etching processes. This plasma etching is then generally carried out before the glass etching. To this end, a plurality of wafers are stacked one on top of the other, and the outside edges are exposed to the plasma. The plasma is
30 fed with fluorinated gases, for example tetrafluoromethane. The reactive species occurring on plasma decomposition of these gases etch the edges of the wafer. In general, the plasma etching is then followed by the glass etching.

35 4. Coating of the front side with an antireflection layer

After the etching of the glass and the optional edge insulation, the front side of the later solar cells is coated with an antireflection coating, which usually consists of amorphous and hydrogen-rich silicon nitride. Alternative anti-reflection coatings are conceivable. Possible coatings can be titanium dioxide, magnesium fluoride, tin dioxide and/or consist of corresponding stacked layers of silicon dioxide and silicon nitride. However, antireflection coatings having a different composition are also technically possible.

The coating of the wafer surface with the above-mentioned silicon nitride essentially fulfils two functions:

- on the one hand the layer generates an electric field owing to the numerous incorporated positive charges, which can keep charge carriers in the silicon away from the surface and can considerably reduce the recombination rate of these charge carriers at the silicon surface (field-effect passivation),
- on the other hand this layer generates a reflection-reducing property, depending on its optical parameters, such as, for example, refractive index and layer thickness, which contributes to it being possible for more light to be coupled into the later solar cell.

The two effects can increase the conversion efficiency of the solar cell. Typical properties of the layers currently used are: a layer thickness of ~80 nm on use of exclusively the above-mentioned silicon nitride, which has a refractive index of about 2.05. The antireflection reduction is most clearly apparent in the light wavelength region of 600 nm. The directed and undirected reflection here exhibits a value of about 1% to 3% of the originally incident light (perpendicular incidence to the surface perpendicular of the silicon wafer).

The above-mentioned silicon nitride layers are currently generally deposited on the surface by means of the direct PECVD process. To this end, a plasma into which silane and ammonia are introduced is ignited in an argon gas atmosphere. The silane and the ammonia are reacted in the plasma via ionic and free-radical reactions to give silicon nitride and at the same time deposited on the wafer surface. The properties of the layers can be adjusted and controlled, for example, via the individual gas flows of the reactants. The

deposition of the above-mentioned silicon nitride layers can also be carried out with hydrogen as carrier gas and/or the reactants alone. Typical deposition temperatures are in the range between 300°C and 400°C. Alternative deposition methods can be, for example, LPCVD and/or sputtering.

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5. Production of the front-side electrode grid

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After deposition of the antireflection layer, the front-side electrode is defined on the wafer surface coated with silicon nitride. In industrial practice, it has become established to produce the electrode with the aid of the screen-printing method using metallic sinter pastes. However, this is only one of many different possibilities for the production of the desired metal contacts.

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In screen-printing metallisation, a paste which is highly enriched with silver particles (silver content $\geq 80\%$) is generally used. The sum of the remaining constituents arises from the rheological assistants necessary for formulation of the paste, such as, for example, solvents, binders and thickeners. Furthermore, the silver paste comprises a special glass-frit mixture, usually oxides and mixed oxides based on silicon dioxide, borosilicate glass and also lead oxide and/or bismuth oxide. The glass frit essentially fulfils two functions: it serves on the one hand as adhesion promoter between the wafer surface and the mass of the silver particles to be sintered, on the other hand it is responsible for penetration of the silicon nitride top layer in order to facilitate direct ohmic contact with the underlying silicon. The penetration of the silicon nitride takes place via an etching process with subsequent diffusion of silver dissolved in the glass-frit matrix into the silicon surface, whereby the ohmic contact formation is achieved. In practice, the silver paste is deposited on the wafer surface by means of screen printing and subsequently dried at temperatures of about 200°C to 300°C for a few minutes. For completeness, it should be mentioned that double-printing processes are also used industrially, which enable a second electrode grid to be printed with accurate registration onto an electrode grid generated during the first printing step. The thickness of the silver metallisation is thus increased, which can have a positive influence on the conductivity in the electrode grid. During this drying, the solvents present in the paste are expelled from the paste. The printed wafer subsequently passes through a belt furnace. A furnace of this type generally

has a plurality of heating zones which can be activated and temperature-controlled independently of one another. During passage through the belt furnace, the wafers are heated to temperatures up to about 950°C. However, the individual wafer is generally only subjected to this peak temperature for a few seconds. During the remainder of the passing phase, the wafer has temperatures of 600°C to 800°C. At these temperatures, organic accompanying substances present in the silver paste, such as, for example, binders, are burnt out, and the etching of the silicon nitride layer is initiated. During the short time interval of prevailing peak temperatures, the contact formation with the silicon takes place. Then the wafers are allowed to cool down.

The contact formation process outlined briefly in this way is usually carried out simultaneously with the two remaining contact formations (cf. 6 and 7), which is why the term co-firing process is also used in this case.

The front-side electrode grid consists per se of thin fingers (typical number ≥ 68) which have a width of typically 80 μm to 140 μm , and also busbars having widths in the range from 1.2 mm to 2.2 mm (depending on their number, typically two to three). The typical height of the printed silver elements is generally between 10 μm and 25 μm . The aspect ratio is rarely greater than 0.3.

6. Production of the back busbars

The back busbars are generally likewise applied and defined by means of screen-printing processes. To this end, a similar silver paste to that used for the front-side metallisation is used. This paste has a similar composition, but comprises an alloy of silver and aluminium in which the proportion of aluminium typically makes up 2%. In addition, this paste comprises a lower glass-frit content. The busbars, generally two units, are printed onto the back of the wafer by means of screen printing with a typical width of 4 mm and compacted and sintered as already described under point 5.

7. Production of the back electrode

The back electrode is defined after the printing of the busbars. The electrode material consists of aluminium, which is why an aluminium-containing paste is printed onto the remaining free area of the wafer back by means of screen printing with an edge separation < 1 mm for definition of the electrode. The paste is composed of $\geq 80\%$ of aluminium. The remaining components are those, which have already been mentioned under point 5 (such as, for example, solvents, binders, etc.). The aluminium paste is bonded to the wafer during the co-firing by the aluminium particles beginning to melt during the warming and silicon from the wafer dissolving in the molten aluminium. The melt mixture functions as dopant source and releases aluminium to the silicon (solubility limit: 0.016 atom per cent), where the silicon is p^+ -doped as a consequence of this alloying and indiffusion. During cooling of the wafer, a eutectic mixture of aluminium and silicon, which solidifies at 577°C and has a composition having a mole fraction of 0.12 of Si, deposits, inter alia, on the wafer surface.

As a consequence of the indiffusion of aluminium into the silicon, a highly doped p-type layer, which functions as a type of mirror ("electric mirror") on parts of the free charge carriers in the silicon, forms on the back of the wafer. These charge carriers cannot overcome this potential wall and are thus kept away from the back wafer surface very efficiently, which is thus evident from an overall reduced recombination rate of charge carriers at this surface. This potential wall is generally referred to as back surface field.

The sequence of the process steps described under points 5, 6 and 7 can, but does not have to, correspond to the sequence outlined here. It is evident to the person skilled in the art that the sequence of the outlined process steps can in principle be carried out in any conceivable combination.

8. Optional edge insulation

If the edge insulation of the wafer has not already been carried out as described under point 3, this is typically carried out with the aid of laser-beam methods after the co-firing. To this end, a laser beam is directed at the front of the solar cell, and the front-side p-n junction is parted with the aid of the energy coupled in by this beam. Cut trenches having a depth of up to $15\text{ }\mu\text{m}$

are generated here as a consequence of the action of the laser. Silicon is removed from the treated site here via an ablation mechanism or thrown out of the laser trench. This laser trench typically has a width of 30 μm to 60 μm and is about 200 μm away from the edge of the solar cell.

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After production, the solar cells are characterised and classified in individual performance categories in accordance with their individual performances.

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The person skilled in the art is aware of solar-cell architectures with both n-type and also p-type base material. These solar cell types include, inter alia,

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- PERC solar cells
- PERL solar cells
- PERT solar cells
- MWT-PERT and MWT-PERL solar cells derived therefrom
- bifacial solar cells
- back junction contact cells
- back junction contact cells with interdigital contacts.

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Object of the present invention

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Nowadays, most of the manufacturers of displays or electronics are trying to reduce the consumption and the referring total emission of chemicals in order to prevent the environmentally pollution. At the same time they try to achieve the same or improved process results, for example to produce deeper etched structures with higher resolution in a shorter process time.

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In this context one big challenge of this development is the introduction of a reasonable patterning method of transparent conductive oxide layer (TCO layers) as well as of Si, SiO₂, SiN_x layers in mass production.

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Thus, the object of the present invention is to provide an inexpensive, simple and fast etching process for the patterning of Si, SiO₂, SiN_x, or transparent conductive oxide layers with reduced need for chemicals and a decreased total emission of chemicals into the environment. A further object of the present invention is to provide a suitable method for patterning of Si, SiO₂,

SiN_x, or transparent conductive oxide layers on inorganic or flexible polymer substrates with high accuracy.

5 But what is also needed, is a process for reproducibly patterning a wide variety of substrates with a lateral dimension of 80 μm or less, preferably less than 50 μm. The processes should be low-cost, highly reproducible and scalable.

Subject-matter of the invention

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Inexpectedly it was found that superabsorbing particles can be used for etching compositions with improved etching rates.

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More specifically, the present invention relates to etching compositions for etching of surfaces consisting of Si, SiO₂, SiN_x or of transparent conductive oxides (TCO), comprising an etchant based on phosphoric acid, salts of phosphoric acid or adducts of phosphoric acid or a mixture of phosphoric acid, salts of phosphoric acid and/or adducts of phosphoric acid, and/or hydrochloric acid and/or hydrofluoric acid in combination with a

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superabsorbing compound. Most preferably the added superabsorbing compounds are porous particles and are based on crosslinked sodium polyacrylates. But also superabsorbing compounds may be added as long as they are stable against the comprising etchant.

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The present invention also relates to the use of these new etching compositions.

In particular, the present invention relates also to a method as claimed by claims 8 to 13.

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Detailed Description of the Invention

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In general, if there is a need to increase the etching rate or depth, the etching temperature and/or time is increased. But this measure is promising only to a certain degree. When the entire water contained in the etching paste is consumed during the etching process, the process will stop after a

certain time. If the etching step is supported by heating then the etching step is finished much earlier because of water loss by evaporation. This means, that especially the contained water is one of the limiting factors for the etching "power" of an etching paste.

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Since after application of the compositions from the outside the water content cannot be changed subsequently, in the last few years the developments have been so that water-containing gels have been developed, in which network-forming inorganic or organic additives are used to thicken the compositions and to include as much water as possible.

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In the past, attempts have also been made to extend the duration of the etching process by the addition of low-melting and compatible resins to the etching pastes, which float during the heating step and form a dense layer to water vapor and prevent the water loss from the etching paste during etching.

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However, this has the disadvantage that complicated purification steps are required after the etching step, since residues of the molten polymer resins must be removed from the treated surfaces.

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Now, it has been found, that by the addition of special polymers, which are traded as superabsorbents, etching and doping results can be greatly improved.

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Superabsorbent polymers

The term "superabsorbent polymer" means a polymer that is capable in its dry form of spontaneously absorbing at least 20 times its own weight of aqueous fluid, in particular of water and especially distilled water. Such superabsorbent polymers are described in the publication "Absorbent polymer technology, Studies in polymer science 8" by L. Brannon- Pappas and R. Harland, published by Elsevier, 1990.

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These polymers have a large capacity for absorbing and retaining water and aqueous fluids. After absorption of the aqueous liquid, the polymer particles thus engorged with aqueous fluid remain insoluble in the aqueous fluid and thus conserve their individualized particulate state.

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Superabsorbers are polymers, which are commercially available being composed of polyacrylates in form of non-toxic spherical particles, being capable of absorbing and retaining many times their weight in water. They have a unique surface cross-linking chemistry, which prevents gel-blocking and allows liquid to flow freely to the particles for efficient absorption. At the same time, they thicken fluids and turn them into a solid gel, and swell when in contact with liquid, and exchange ions during absorption. At present these superabsorbers are used for example for the production of baby diapers or for improving poor quality of soil and water and unfavorable environment where they are used for maintaining water and for providing uniform supply of water to plants.

As such, known superabsorbent polymers may have a water-absorbing capacity ranging from 20 to 2000 times its own weight (i.e. 20 g to 2000 g of absorbed water per gram of absorbent polymer), preferably from 30 to 1500 times and better still from 50 to 1000 times. These water absorption characteristics are defined under standard temperature (25°C) and pressure (760 mmHg, i.e. 100 000 Pa) conditions and for distilled water.

The value of the water-absorbing capacity of a polymer may be determined by dispersing 0.5 g of polymer(s) in 150 g of a water solution, waiting for 20 minutes, filtering the unabsorbed solution through a 150 µm filter for 20 minutes and weighing the unabsorbed water. The superabsorbent polymer used in the composition of the invention is in the form of particles. Preferably, the superabsorbent polymer has, in the dry or nonhydrated state, an average size of less than or equal to 100 µm, preferably less than or equal to 50 µm, ranging for example from 10 to 100 µm, preferably from 15 to 50 µm, and better still from 20 to 30 µm.

The average size of the particles corresponds to the weight-average diameter (D₅₀) measured by laser particle size analysis or another equivalent method known to those skilled in the art.

These particles, once hydrated, swell and form soft particles, which have an average size that can range from 10 µm to 1000 µm.

Preferably, the superabsorbent polymers used in the present invention are in the form of spherical particles.

The superabsorbent polymers may be chosen from :

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- crosslinked sodium polyacrylates, for instance those sold under the names Octacare[®] X100, X1 10 and RM100 by the company Avecia[®], those sold under the names Flocare[®], GB300 and Flosorb 500 by the company SNF, those sold under the names Luquasorb[®] 1003, Luquasorb[®] 1010,
10 Luquasorb[®] 1280 and Luquasorb[®] 1110 or Artic Gel[®] by the company BASF, FAVOR[®] by the company Evonik, and those sold under the names Water Lock[®] G400 and G430 (INCI name: Acrylamide/Sodium acrylate copolymer) by the company Grain Processing, or else Aquakeep[®] 10 SH NF proposed by the company Sumitomo Seika,

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- starches grafted with an acrylic polymer (copolymer) and in particular with sodium polyacrylate, such as those sold under the name Sanfresh[®] ST-100MC by the company Sanyo Chemical Industries or Makimousse[®] 25 or Makimousse[®] 12 by the company Daito Kasei (INCI name: Sodium
20 polyacrylate Starch),

- hydrolyzed starches grafted with an acrylic polymer (homopolymer or copolymer) and especially the acryloacrylamide/sodium acrylate copolymer, such as those sold under the names Water Lock[®] A-240, A-180, B-204, D-
25 223, A-100, C-200 and D-223 by the company Grain Processing (INCI name: Starch/acrylamide/sodium acrylate copolymer),

- polymers based on starch, on gum and on cellulose derivative, such as the product containing starch, guar gum and sodium carboxymethylcellulose,
30 sold under the name Lysorb[®] 220 by the company Lysac,

- and mixtures thereof.

The superabsorbent polymers used in the present invention may be
35 crosslinked or noncrosslinked. They are preferably chosen from the group of crosslinked polymers.

The preparation of superabsorbent acrylic acid polymers is effected by polymerization of acrylic acid with a "cross-linker" (crosslinker), that is, a compound having two or more double bonds. This is most often carried out as a solution polymerization. Redox systems such as $K_2S_2O_8$ / $Na_2S_2O_5$ or hydrogen peroxide / ascorbate are common and inexpensive initiators for this polymerization. By the added cross-linker crosslinks are created between the individual polymer chains, which results in the insolubility of the polymer. Preferably diacrylate, allylmethacrylate, triallylamines or tetraallyloxyethane are used as crosslinkers. Other suitable crosslinkers are i. e. ethyleneglycol diacrylate or 1,1,1-trimethylolpropane-triacrylate. When enough chains are linked together and a macromolecular network is formed, the system converts from a viscous mass into an elastic solid ("gel point"). The amount of crosslinking substances determines the water absorption capacity of the gel. However, a high crosslink density limits the possibility of expansion of the polymer backbone. The insoluble superabsorbent particles are after synthesis in porous granules. These particles are not hygroscopic despite of their high affinity for water, so their storage and transport are unproblematic.

Thus, as already mentioned, preferably the superabsorbent polymers used in the present invention are crosslinked acrylic homopolymers or copolymers, which have preferably been neutralized, and which are in particulate form. Preferably, the superabsorbent polymer is chosen from crosslinked sodium polyacrylates, preferably in the form of particles with an average size (or average diameter) of less than or equal to 100 microns, more preferably in the form of spherical particles. These polymers preferably have a water-absorbing capacity of from 10 to 100 g/g, preferably from 20 to 80 g/g and better still from 40 to 80 g/g.

The superabsorbent polymer(s) may be present in the etching compositions according to the present invention in a concentration ranging, for example, from 0.05% to 8% by weight, preferably from 0.05% to 5% by weight and preferably ranging from 0.05% to 1 % by weight, relative to the total weight of the composition.

These preferred superabsorbers have a glass transition temperature of about 140°C. If they are heated to higher temperatures they decompose.

The latter property is advantageous in etching compositions used in a process for etching and doping in one process step.

5 According to the present invention a superabsorber is saturated with water, then the superabsorber is added to the etching paste to act as a water spender during the etching process. The duration of the actual etching process may be increased, what results in a significantly increased etching depth. The paste is screen printed on a silicon wafer, which is heated then up to 450°C for 2 min. After the heating step the wafer may be cleaned with
10 DI water. Another option is to increase the temperature for a short time at a level where a doping of the treated surface takes place. While in the beginning added superabsorbing particles spend their water for an increased etching duration, these particles decompose at higher temperatures and, if desired, an additionally doping can be processed at areas where the etching
15 paste is applied. After etching and doping the surfaces are simply cleaned with water.

Another embodiment of the manufacturing process of the present invention is to increase the cell efficiency of the bifacial solar cells, and creating a
20 selective back surface field (S-BSF). The S-BSF can be created by structuring an n-type wafer with a deep phosphor diffused back side which is etched back selectively with an etching paste. This method is already used to form a selective emitter on the front side, but on the front side only 30 – 70 nm of silicon has to be removed. For the formation of a selective back
25 surface field on the backside more than 150 nm of this layer has to be removed. But this is not possible with the current standard etching pastes, because the etching rate in silicon is not sufficient.

Advantageously the etching paste according to the present invention can
30 also be used for other applications in semiconductor and display production steps where a high etching rate is necessary, i.e. for structuring of SiN_x -, SiO_2 -, passivation or TCO- layers. Furthermore, compositions as disclosed here support the printing with high resolution by various methods, because the added particulate superabsorber act as thickener and as water spender
35 for the etching reaction. In addition, it is possible by the present compositions to perform different etching depths with the same base paste in the same

etching time, so that, if appropriate, different settings of the process equipment used may be omitted.

5 In order to demonstrate the effectiveness of the pastes of the invention the pastes have been compared with conventional compositions. The results clearly show the improved etching depths achieved by etching compositions comprising superabsorbing particles.

10 For example Figure 1 shows Electrochemical Capacitance Voltage (ECV) profiles of n-type wafers with phosphor diffused backside, before and after etching. In this figure corresponding diffusion profiles of a non-etched (green), of a substrate etched with a standard etching paste (blue), and of a substrate etched with an etching paste where a superabsorber saturated with water (green) was added. The curves, which are shown in Figure 1, clearly
15 demonstrate that the etching depth is increased by 90 nm when a superabsorber is added to the paste composition.

20 **Sheet resistivity measurement**

Etching paste	Sheet resistivity
Non-etched	20 Ohm/sq.
Standard SE3000	38 Ohm/sq.
25 CL15.55 (with Superabsorber)	64Ohm/sq.

Table 1: Four point probe resistivity measurements of structured substrates

30 In Table 1 it is shown that the sheet resistivity is significantly increased from 38 to 64 Ohm/sq, if the etching paste according to the present invention is used for carrying out the method for structuring substrate surfaces.

35 As already described above, the method disclosed here may be performed both at industrial as well as in micro-scale. The user is free in the manner of carrying out the etching method. It is self-explanatory that depending on the nature of the surfaces differently composed etching compositions are to be

applied and, one or the other composition of the added superabsorber in form of porous polymer particles may be advantageous in combination with the selected etching composition. Here the expert has the choice between porous polymers made from sodium polyacrylates, polyvinyl pyrrolidone, natural polymers, like Amylopektin, starch, guar gum, gelatine, cellulose, and sodium carboxymethylcellulose and its derivatives as addressed above and which are cross-linked or non-cross-linked. As there are different suberabsorbers in form of granules or spherical particles commercially available one of ordinary skill in the art can readily identify the most suitable superabsorber beads for producing an etching composition which is most suitable for the desired application.

The present description enables one of ordinary skill in the art to practice the present invention comprehensively. Even without further comments, it is therefore assumed that a person of ordinary skill in the art will be able to utilise the above description in the broadest scope.

If anything is unclear, it is understood that the publications and patent literature cited and known to the artisan should be consulted. Accordingly, cited documents are regarded as part of the disclosure content of the present description.

For better understanding and in order to illustrate the invention, examples are presented below which are within the scope of protection of the present invention. These examples also serve to illustrate possible variants.

Furthermore, it goes without saying to one of ordinary skill in the art that, both in the examples given and also in the remainder of the description, the component amounts present in the compositions always only add up to 100% by weight or mol%, based on the composition as a whole, and cannot exceed this percentage, even if higher values could arise from the per cent ranges indicated. Unless indicated otherwise, % data are therefore % by weight or mol%, with the exception of ratios, which are shown in volume data.

35

Examples

Example 1

- 5 parts phosphoric acid (85%)
3 parts diethylenglycolmonoethylether (DEGMEE)
5 2 parts dimetyhlensulfoxid
1 part polyvinypyrrolidon
1 part DI water

- 10 To this mixture 1 weight-% Superabsorber (saturated with DI water) and 3 parts
Ceridust 9202 F. Then the whole mixture is stirred for 2hours.

Example 2

- 8parts phosphoric acid (85%)
15 3parts diethylenglycolmonoethylether (DEGMEE)
2parts dimetyhlensulfoxid
1part polyvinypyrrolidon
1part DI water

- 20 To this mixture 1 weight-% Superabsorber (saturated with DI water) and 3 parts
Ceridust 9202 F. Then the whole mixture is stirred for 2hours.

25 Example 3

- 6parts phosphoric acid (85%)
3parts diethylenglycolmonoethylether (DEGMEE)
3parts dimetyhlensulfoxid
30 1part polyvinypyrrolidon
1part DI water

- To this mixture 1 weight-% Superabsorber (saturated with DI water) and 3 parts
Ceridust 9202 F. Then the whole mixture is stirred for 2hours.

35

Example 4

- 5 6parts phosphoric acid (85%)
3parts diethylenglycolmonoethylether (DEGMEE)
3parts dimetyhlensulfoxid
1part polyvinypyrrolidon
2parts DI water

To this mixture 0.5 weight-% Superabsorber (satured with DI water) and 3 parts Ceridust 9202 F. Then the whole mixture is stirred for 2hours.

10 Example 5

- 15 6parts phosphoric acid (85%)
3parts diethylenglycolmonoethylether (DEGMEE)
3parts dimetyhlensulfoxid
1part polyvinypyrrolidon

To this mixture 5 weight-% Superabsorber (satured with DI water) and 3 parts Ceridust 9202 F. Then the whole mixture is stirred for 2hours.

20 Example 6

- 25 6 parts phosphoric acid (85%)
3 parts diethylenglycolmonoethylether (DEGMEE)
3 parts n-methylpyrrolidon
1 part polyvinypyrrolidon

To this mixture 5 weight-% Superabsorber (satured with DI water) and 3 parts Ceridust 9202 F. Then the whole mixture is stirred for 2hours.

30 Structuring of the substrate

- 35 This finished etching paste is printed with a screen printer on a phosphor diffused silicon wafer (Figure 3). Then the wafer is heated on a hotplate for 2 minutes at a temperature of about 450°C (Figure 4). After the heating step the paste is removed by rinsing with DI water and subsequently drying with

compressed air. These process steps result in a structured substrate with S-BSF (Figure 6).

5 The process is illustrated by the following figures with reference to the structuring results of the process steps in the production of an n-type solar cell.

List of Figures:

10

The different figures 1 – 5 schematically show the different states of the treated substrate surface corresponding to the successive process steps:

15

Figure 1: ECV profiles of n-type wafers with phosphor diffused backside, before and after etching.

Figure 2: n-Type solar cell with a deep uniform back surface field

20

Figure 3: The etching paste is printed on the substrate

Figure 4: The etching process is activated by heat and the P-BSF is structured

25

Figure 5: The substrate with a Selective Back Surface Field (high and low diffused areas).

Figure 6: Screenprinted n-type solarcell with a S-BSF

30

35

What is claimed

1. Etching composition for the etching of surfaces consisting of Si, SiO₂, SiN_x or transparent conductive oxides (TCO), comprising an etchant
5 based on phosphoric acid, salts of phosphoric acid or adducts of phosphoric acid or a mixture of phosphoric acid, salts of phosphoric acid and/or adducts of phosphoric acid, and/or hydrochloric acid and/or hydrofluoric acid in combination with a superabsorbing compound.
- 10 2. Etching composition according to claim 1 comprising a porous particulate superabsorbing compound based on sodium polyacrylate.
3. Etching composition according to claim 1 or 2 wherein the etchant is based on potassium hydroxide.
15
4. Etching composition according to claim 1 or 2, wherein the etchant is based on hydrochloric acid or hydrofluoric acid.
5. Etching composition according to one or more of the claims 1 to 4,
20 comprising at least one solvent, optionally an organic and/or inorganic thickener, and/or binders and/or crosslinking agents, and optionally additives selected from the group of defoaming agents, thixotropic agents, wetting agents, degassing agents, ammonium salts, like triethylene ammonium chloride.
25
6. Use of an etching composition according to one or more of the claims 1 - 5 in a method for structuring a substrate surface wherein the composition is applied onto the surface by via, spraying, screenprinting, spincoating, tamponprinting, inkjetprinting, stencilprinting, or dispensing.
30
7. Use of an etching composition according to one or more of the claims 1 - 5 in a method for structuring a substrate surface wherein the composition is applied to the surface by screenprinting.
- 35 8. Method for etching a substrate surface consisting of Si, SiO₂, SiN_x or transparent conductive oxides (TCO), wherein an etching composition

according to one or more of the claims 1 – 5 is applied over either the entire surface or selectively onto the surface followed by heating of the substrate via hotplate, IR radiation, microwave oven, convection furnace or UV irradiation.

5

9. Method according to claim 7 for the production of solar cells, wherein an etching composition according to one or more of the claims 1 – 5 is applied over either the entire surface or selectively onto a surface consisting of silicon, silicon oxide or silicon nitride.

10

10. Method according to claim 7 or claim 8 for manufacturing passivation layers in electronic devices, wherein an etching composition according to one or more of the claims 1 – 5 is applied onto a surface consisting of SiN_x or of a transparent metal oxide, like AlO_x .

15

11. Method according to one of the claims 8, 9 or 10 for the production of solar cells, wherein an etching composition according to one or more of the claims 1 – 4 is applied onto a surface consisting of transparent conductive oxides (TCO).

20

12. Method according to claim 8 or claim 9 for the production of displays, wherein an etching composition according to one or more of the claims 1 – 4 is applied onto a surface consisting of Si, SiO_2 , SiN_x or transparent conductive oxides (TCO).

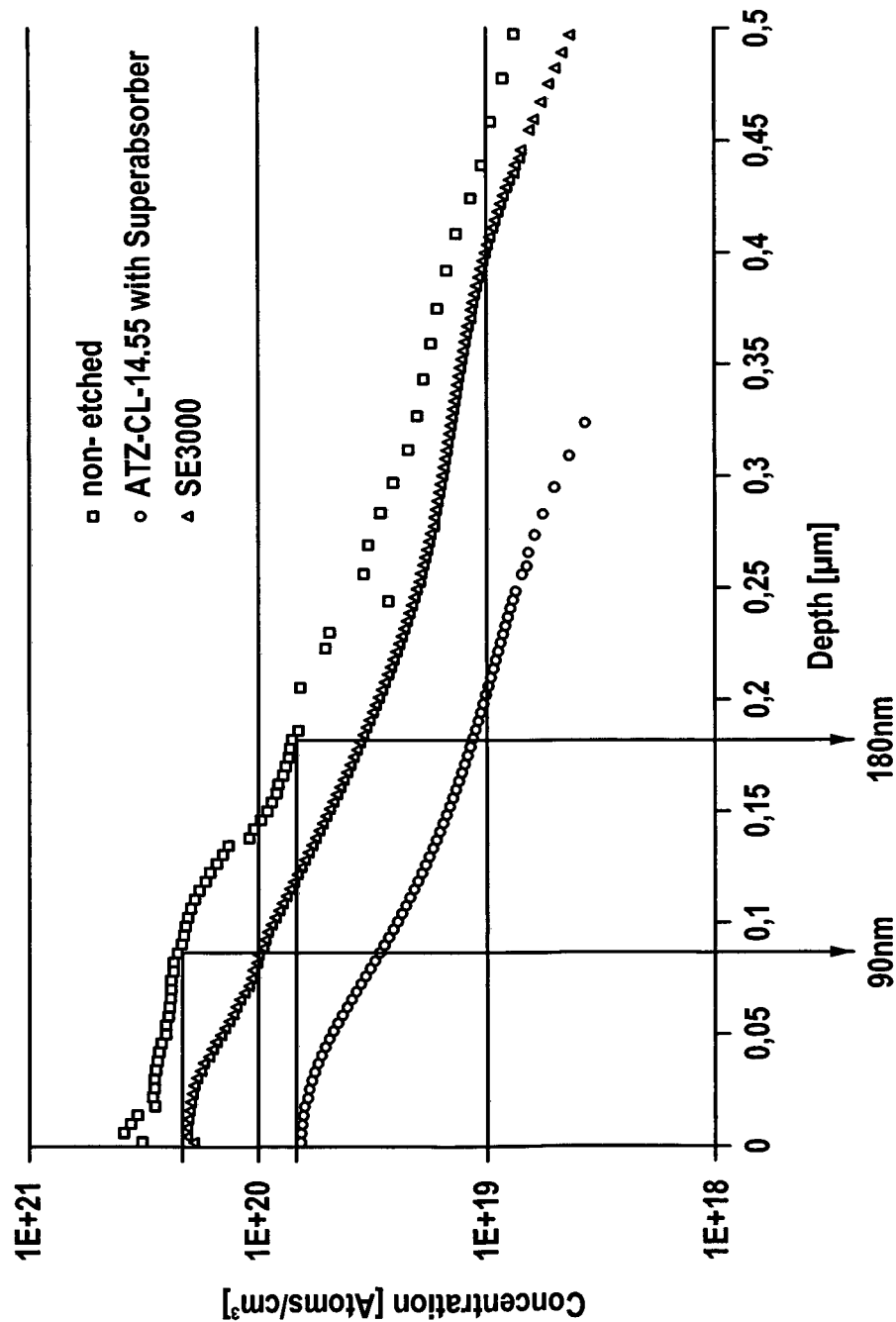
25

13. Method according to claims 8 or 9 for the production of solar cells, wherein an etching composition according to one or more of the claims 1 – 4 is applied onto a surface consisting of SiN_x or of a transparent metal oxide, like AlO_x for structuring and passivation.

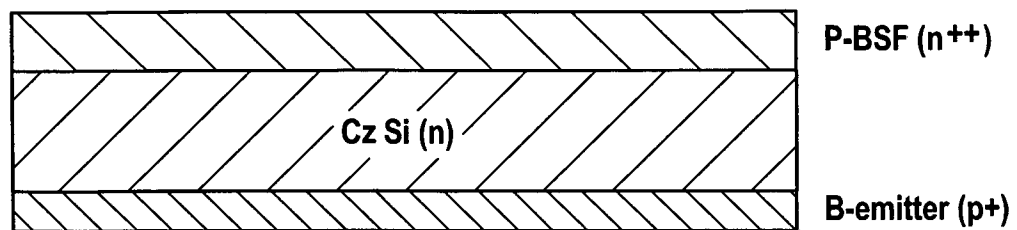
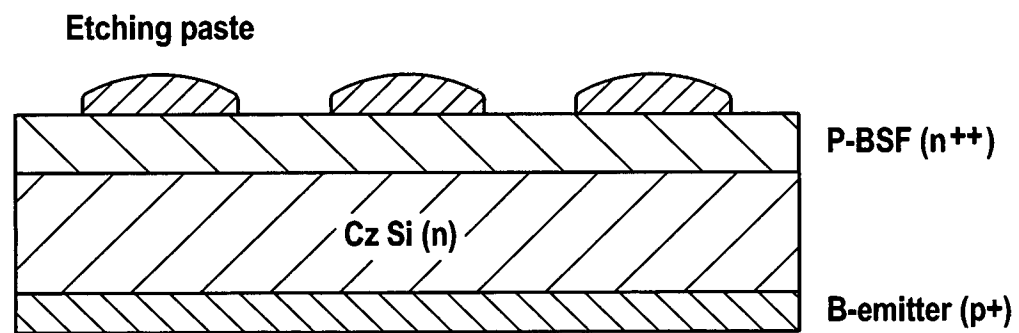
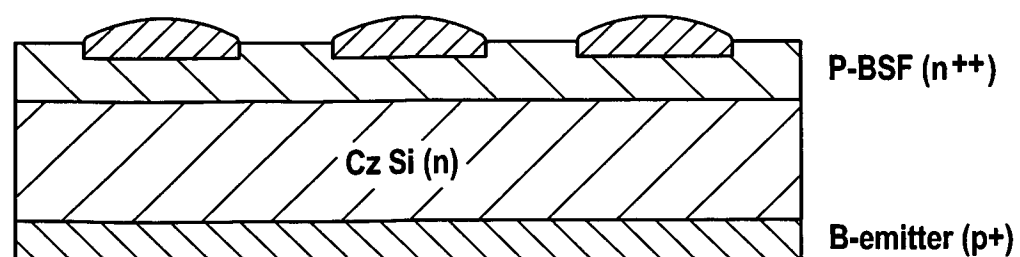
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35

Fig. 1



2 / 3

Fig. 2**Fig. 3****Fig. 4**

3 / 3

Fig. 5

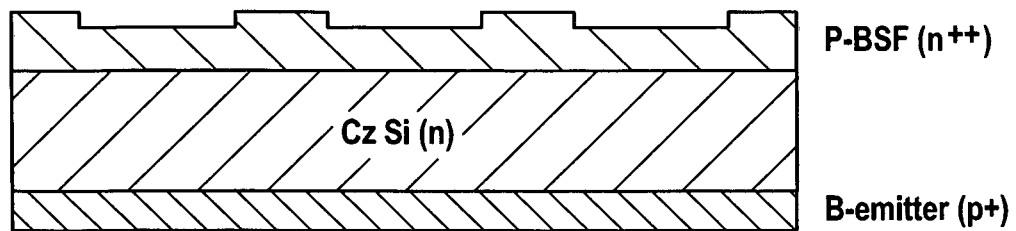
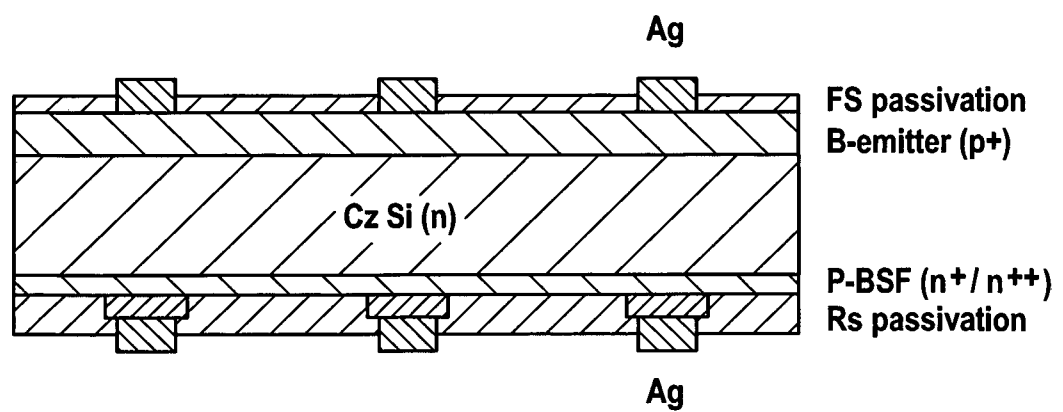


Fig. 6



INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2015/002353

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 3(completely); 1, 2, 4-13(partially)
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/002353

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K13/06 C09K13/08 H01L21/3213 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)
C09K 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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 434 536 A1 (STELLA CHEMIFA CORP [JP]) 28 March 2012 (2012-03-28) claims 1,2,5 paragraph [0040] -----	1,2,4,6, 10-13
X	US 2014/021400 A1 (COENJARTS CHRISTOPHER [US]) 23 January 2014 (2014-01-23) claims 1,3,18,37-39 paragraph [0094] - paragraph [0099] -----	1,2,5-13
A	US 2008/210660 A1 (STOCKUM WERNER [DE] ET AL) 4 September 2008 (2008-09-04) the whole document -----	1,2,4-13
A	WO 2013/182265 A1 (MERCK PATENT GMBH [DE]) 12 December 2013 (2013-12-12) the whole document -----	1,2,4-13



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

21 January 2016

Date of mailing of the international search report

28/01/2016

Name and mailing address of the ISA/

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Authorized officer

Domínguez Gutiérrez

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2015/002353

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
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			WO	2007003255 A1		11-01-2007

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			TW	201400592 A		01-01-2014
			US	2015152328 A1		04-06-2015
			WO	2013182265 A1		12-12-2013

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 3(completely); 1, 2, 4-13(partially)

Claim 1 relates to an etching composition comprising (i) an etchant, and (ii) a superabsorbing compound.

According to the description, a superabsorbing compound means a polymer that is capable in its dry form of spontaneously absorbing an aqueous fluid. Insofar as the concept water-absorbing polymer implies, it is noted that this constitutes a state-of-the-art on its own, spanning a large number of compounds that are not covered in the present application, in which merely polyacrylates are mentioned.

Therefore, claim 1 is not supported by the description as required by Article 6 PCT because its scope is broader than justified by the description and drawings. The subject-matter of claim 1 envisages any superabsorbing compound, which is not commensurate with the contribution made to the art. Furthermore, it is not plausible that all materials susceptible of falling under the concept of superabsorbing compounds would provide the required technical effect.

Considering this lack of support, the non-compliance with the substantive provisions is to such an extent, that the search has to be performed taking into consideration the non-compliance in determining the extent of the search of claim 1-15 (PCT Guidelines 9.19 and 9.23). The search of this claim was restricted to those claimed combinations of compounds which appear to be plausible and supported, namely where the superabsorbing compound is a superabsorbent polymer according to a compound recited in claim 2 and the description, page 16, lines 4-32.

Claim 3 does not fulfill the requirements of Art. 6 PCT because its current wording reads that the etchant is based on potassium hydroxide, whereas the etchants recited in claim 1 are strong inorganic acids. It is not clear how an acidic-based etching composition can be based on potassium hydroxide.

The description remains silent on this aspect, potassium hydroxide is exclusively mentioned in the introductory portion, leaving no means of further interpreting this claim. There are those no evidences of how this aspect can be plausibly supported in the further prosecution of the application.

Thus, claim 3 as a whole is not in compliance with the provisions of clarity within the meaning of Article 6 PCT, as it is particularly burdensome for a skilled person to establish the subject-matter for which protection is sought. The non-compliance with the substantive provisions is to such an extent, that the search was performed taking into consideration the non-compliance in determining the extent of the search (PCT Guidelines 9.19 and 9.25).

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.