

Alkaline Solution for Texturing Monocrystalline Silicon Substrate

Field of Invention

5 **[001]** The present invention relates to an alkaline solution for texturing monocrystalline silicon substrate in the manufacture of solar cells.

Background

10 **[002]** (100) surface orientated crystalline silicon wafers are usually used for manufacturing silicon solar cell. Etching of silicon is highly anisotropic and this (100)-orientated wafers is advantageous in that the $\langle 111 \rangle$ planes act as etch stops layers and etching of the $\langle 100 \rangle$ and $\langle 110 \rangle$ -crystal planes form square-based pyramids with $\langle 111 \rangle$ inclined surfaces. These pyramidal structures enhance light trapping by multiple reflections, thereby increase coupling of light into a solar cell. This approach of forming pyramidal structures or texture
15 on the surface of the silicon wafer has been used to increase performance of solar energy conversion in monocrystalline solar cells.

20 **[003]** Known techniques of texturing monocrystalline silicon wafer involves immersing the wafers in sodium or potassium hydroxide, isopropyl alcohol (IPA) and glycol at a temperature range of about 65 to 95 degree C. However, this solution suffers from a high rate of evaporation of the IPA and high waste disposal costs for the spent chemicals. In addition, the pyramidal texture obtained with known IPA based hydroxide texturing solution is generally large. As can be seen in FIG. 1A, the pyramidal texture is generally larger than about 5 micron at the base of the pyramidal structure. FIG. 1B shows
25 distribution of the pyramidal texture.

30 **[004]** US Patent No. 6,197,611 issued to Mitsubishi Denki KK describes the use of a silicon etching chemical containing sodium carbonate at a temperature range of about 80 – 100 degree C. This approach promises highly uniform silicon texturing at low production costs by doing away with the use of IPA.

[005] Despite development of many silicon texturing solutions, there still exists a need for another type of chemical recipe for texturing monocrystalline silicon wafers, especially with the general push for improving solar cell performance and lowering manufacturing costs.

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Summary

[006] The following presents a simplified summary to provide a basic understanding of the present invention. This summary is not an extensive overview of the invention, and is not intended to identify key features of the invention. Rather, it is to present some of the inventive concepts of this invention in a generalised form as a prelude to the detailed description that is to follow.

[007] The present invention provides an alkaline texturing solution for texturing monocrystalline silicon substrate to increase coupling of light into a solar cell. This has been shown by the lower reflectance characteristics of mono-crystalline silicon substrates textured according to the present invention and performance of solar cells made from these textured silicon substrates.

[008] In one embodiment, the present invention provides an alkaline solution for forming pyramidal texture on mono-crystalline silicon substrate, said solution comprising: an aqueous solution of about 0.5% to about 3% by weight of hydroxide; and dissolved silicon in the range of about 10 g/L to about 45 g/L.

[009] Preferably, the concentration of the dissolved silicon ranges from about 20 g/L to about 40 g/L and the hydroxide is sodium or potassium hydroxide. In use, a silicon wafer is immersed in said texturing solution for a time ranging from about 4 minutes to about 9 minutes to produce generally a pyramidal texture size of about 2-4 microns when said texturing solution is heated between about 65 to about 95 degree C.

[0010] In another embodiment, the present invention provides a method for texturing a mono-crystalline silicon wafer, the method comprising: immersing said mono-crystalline silicon wafer in an aqueous solution of a hydroxide with dissolved silicon for a time ranging from about 4 minutes to about 9 minutes to produce generally a pyramidal texture size of

about 2-4 microns, with said dissolved silicon having a concentration ranging from about 10 g/L to about 45 g/L; and maintaining said aqueous solution at a temperature of between about 65 degree C to about 95 degree C.

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Brief Description of the Drawings

[0011] This invention will be described by way of non-limiting embodiments of the present invention, with reference to the accompanying drawings, in which:

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[0012] FIG. 1A and 1B illustrate scanning electron micrographs at low and high resolutions of a prior art mono-crystalline silicon surface;

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[0013] FIG. 2A illustrates a high-resolution scanning electron micrograph of a textured mono-crystalline silicon surface using a first concentration of texturing solution of the present invention, whilst FIG. 2B illustrates a low-resolution micrograph showing uniform distribution of the textured surface;

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[0014] FIG. 3A illustrates a high-resolution scanning electron micrograph of a textured mono-crystalline silicon surface using a second concentration of the texturing solution of the present invention, whilst FIG. 3B illustrates a low-resolution micrograph showing uniform distribution of the textured surface; and

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[0015] FIG. 4A illustrates reflectance characteristics of a textured mono-crystalline silicon surface using two concentrations of the texturing solution of the present invention compared with reflectance of a conventionally textured mono-crystalline silicon surface. FIG. 4B illustrates reflectance of the same textured mono-crystalline silicon surface over a small spectral range.

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Detailed Description

[0016] One or more specific and alternative embodiments of the present invention will now be described with reference to the attached drawings. It shall be apparent to one skilled in the art, however, that this invention may be practised without such specific details. Some of the details may not be described at length so as not to obscure the invention. For ease of reference, common reference numerals or series of numerals will be used throughout the figures when referring to the same or similar features common to the figures.

[0017] The present invention discloses a wet alkaline texturing solution 100 for forming pyramidal structures on (100)-orientated silicon wafers. This alkaline texturing solution 100 comprises sodium or potassium hydroxide with dissolved silicon. In one embodiment, the hydroxide is in the range of about 0.5% to about 3% by weight and the dissolved silicon is in the range of about 10-45 g/L. FIG. 2A shows a high resolution scanning electron microscope (SEM) micrograph of a monocrystalline silicon wafer that has been chemically textured with the alkaline texturing solution 100 with silicon dissolved at a first concentration of about 10 g/L to about 20 g/L. As seen in FIG. 2A, the pyramidal features are about 3 to about 4 microns at their bases. FIG. 2B shows a micrograph of a low resolution SEM, which shows the uniform distribution of the pyramidal textured surface. FIG. 3A shows a high-resolution scanning electron microscope (SEM) micrograph of a mono-crystalline silicon wafer textured with the alkaline texturing solution 100 with silicon dissolved at a second concentration of about 20 g/L to about 30 g/L. As seen in FIG. 3A, the pyramidal textures are about 2 to about 3 microns at their bases; FIG. 3B shows a micrograph of a low-resolution SEM of the same silicon wafer showing uniform distribution of the pyramidal texture over the silicon wafer surface.

[0018] In one embodiment, preparation of the alkaline texturing solution 100 involves dissolving some silicon in about 0.5% to about 3% by weight of sodium or potassium hydroxide solution. For example, in a first concentration of the alkaline texturing solution 100, five to seven silicon wafers of 125 mm x 125 mm x 200 micron thickness were dissolved in a 0.5-3% by weight of sodium or potassium hydroxide by immersing them in a 3-litre beaker; this yields the first alkaline texturing solution 100 with about 10 g/L to about 20 g/L of dissolved silicon. In a second concentration of the alkaline texturing solution, seven to eight silicon wafers were dissolved in about 0.5-3% by weight of sodium or

potassium hydroxide to give a second alkaline texturing solution 100 concentration with about 20 g/L to about 30g/L of dissolved silicon. In use, a chemically polished silicon wafer is immersed in the texturing solution 100 which is heated to between about 65 degree C to about 95 degree C, preferably in the range of 80-90 degree C, and the texturing time is between about 4 minutes to about 9 minutes to give pyramidal feature sizes of about 2 to about 4 microns on the entire surface of each silicon wafer. During texturing, hydrogen gas is evolved. To ensure uniform texturing, such as streaking that may be caused by release of hydrogen gas, the silicon wafers are mechanically agitated. Alternatively or in addition, the texturing solution is agitated during texturing.

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[0019] The above first and second concentrations of dissolved silicon refer to the starting concentration of the texturing solution 100. During texturing, silicon is continuously dissolved into the alkaline texturing solution. To ensure optimal texturing, inventors found that when the concentration of dissolved silicon reaches about 50 g/L to about 60 g/L, it begins to affect the reflectance characteristic of a textured silicon substrate. With this observation, inventors conclude that the optimal concentration of silicon dissolved in the texturing solution 100 may be kept in the range of about 10 g/L to about 45 g/L. In practice, the texturing solution 100 may be diluted with fresh hydroxide solution to keep the concentration of dissolved silicon to within the range of about 10-45 g/L. Such preparation of the texturing solution 100 by diluting the used texturing solution may be made continuously in a mixing container or made in batches.

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[0020] In another embodiment, silicon balls, instead of silicon wafers, were dissolved in 0.5-3% by weight of hydroxide. The use of silicon balls affects only the time for initial dissolution of silicon into the hydroxide and it does not affect the texturing process time.

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[0021] Prior to texturing of a silicon wafer, each silicon wafer is cleaned, for example, in acetone to remove any organic contaminants that remain on the silicon surface. The cleaning step may be performed with or without an ultrasonic cleaner. This may be followed by rinsing in an alcohol. Each wafer is then rinsed in deionised (DI) water and blown dry with nitrogen gas.

[0022] If the starting wafer surface is not yet chemically polished, there is a layer of mechanical saw damage on the silicon surface. The saw damage layer may contain abraded metal from the saw wire after a wafer is cut from an ingot; the saw damage layer may also contain grinding abrasive when the silicon surface is planarised on a polisher. This saw damage layer is removed by soaking the silicon wafers in a solution of about 20% sodium hydroxide or potassium hydroxide for between about 1 to about 3 minutes. This is followed by neutralisation with 10% hydrochloric acid and a final rinse with DI water.

[0023] In carrying an experiment to verify the present invention, 20 pieces of 125 x 125 mm² monocrystalline silicon wafers with (100) crystal surface were cleaned and chemically polished. 10 of the monocrystalline silicon wafers are then chemically textured by immersing them in the alkaline texturing solution 100 with the first concentration of 10-20 g/L of dissolved silicon whilst the other 10 pieces were immersed in the alkaline texturing solution 100 with the second concentration of 20-30 g/L dissolved silicon. The textured wafers were shipped to a solar cell manufacturing plant for forming the PN junctions, anti-reflection coating and electrodes. The solar cells thus made are then tested for their electrical performance characteristics. Table 1A and 1B shows the electrical performance of 18 solar cells made with silicon wafers textured, respectively, according to the first and second concentrations of the alkaline texturing solution 100 of the present invention when tested under test conditions of 1.5 AM, 1 kW/m² and at a temperature of 25 degree C:

Table 1A:

No.	Efficiency	Fill Factor	Open Circuit Voltage V _{oc} (V)	Short Circuit Current Density, I _{sc} (mA/cm ²)
1	0.156	0.768	0.609	4.968
2	0.158	0.775	0.611	4.959
3	0.158	0.771	0.611	4.991
4	0.159	0.775	0.611	4.992
5	0.157	0.768	0.610	4.976
6	0.152	0.758	0.604	4.936
7	0.146	0.756	0.608	4.721
8	0.147	0.768	0.609	4.683
9	0.143	0.758	0.605	4.648

Table 1B:

No.	Efficiency	Fill Factor	Open Circuit Voltage V_{oc} (V)	Short Circuit Current Density, I_{sc} (mA/cm ²)
1	0.171	0.798	0.612	5.182
2	0.170	0.791	0.617	5.176
3	0.173	0.800	0.618	5.197
4	0.172	0.799	0.618	5.180
5	0.172	0.803	0.619	5.151
6	0.173	0.796	0.618	5.229
7	0.172	0.794	0.619	5.204
8	0.174	0.799	0.620	5.216
9	0.174	0.802	0.620	5.213

[0024] From observation of texture on the silicon wafer surfaces, scattered pyramidal structures were initially formed at the beginning of texturing. As the silicon wafer continued to be immersed in the texturing solution 100, density of the pyramidal texture increased; after about 4 minutes to about 9 minutes, the surface of each silicon wafer is completely textured. From the results shown in Tables 1A-1B and FIGs. 2A-2B, 3A-3B and 4A-4C, it appears that a finer surface texture on the silicon wafer has a great effect on the short circuit current density, I_{sc} and open circuit voltage, V_{oc} of the finally formed solar cell. This short circuit current density, I_{sc} together with the open circuit voltage, V_{oc} and fill factor appear to determine the overall efficiency of a solar cell.

[0025] After the silicon wafers are chemically textured according to the present invention, reflectance of the textured surfaces are measured by a spectroradiometer using a standard 150 mm diameter integrating sphere covering a wavelength range from 200 nm to 2500 nm. FIG. 4A shows reflectance plots of the chemically textured silicon wafer surfaces according to the present invention compared to that of a silicon surfaced textured with conventional NaOH/KOH+IPA recipe. Evidently, from FIG. 4A, the light trapping effectiveness of the silicon wafer surface textured according to the present invention is better than that obtained by conventional texturing chemicals. An advantage of the present invention is the faster rate of texturing with the use of the alkaline solution 100. Another advantage is that the used

texturing solution 100 is not disposed but is refreshed by adding fresh hydroxide solution. The shorter process time and refreshing of used texturing solution 100 contribute to lowering the overall cost of manufacturing solar cells. In addition, the present texturing chemical recipe does not suffer from the variability of IPA concentration of conventional
5 texturing recipe; this means that there is little or no variability in the distribution or density of the pyramidal structures formed with the use of the texturing solution 100. This texturing solution 100 can substitute the conventional texturing chemical with only minor changes, if any, to the existing manufacturing processes.

10 **[0026]** While specific embodiments have been described and illustrated, it is understood that many changes, modifications, variations and combinations thereof could be made to the present invention without departing from the scope of the present invention.

CLAIMS:

1. An alkaline solution for forming pyramidal texture on mono-crystalline silicon substrate, said solution comprising:
an aqueous solution of substantially 0.5% to substantially 3% by weight of hydroxide; and
dissolved silicon in the range of substantially 15 g/L to substantially 45 g/L.
2. An alkaline solution according to claim 1, wherein concentration of the dissolved silicon ranges from substantially 20 g/L to substantially 40 g/L.
3. An alkaline solution according to claim 1 or 2, wherein said hydroxide is sodium or potassium hydroxide.
4. Use of the texturing solution according to any one of claims 1-3, wherein a chemically polished silicon wafer is immersed in said texturing solution for a time ranging from substantially 4 minutes to substantially 9 minutes to produce generally a pyramidal texture size of substantially 2-4 microns when said texturing solution is heated between substantially 65 to substantially 95 degree C.
5. Use according to claim 4, wherein temperature of said texturing solution is maintained between substantially 80 degree C to substantially 90 degree C.
6. A method of texturing a mono-crystalline silicon wafer, said method comprising:
immersing said mono-crystalline silicon wafer in an aqueous solution of substantially 0.5-3% by weight a hydroxide with dissolved silicon for a time ranging from substantially 4 minutes to substantially 9 minutes to produce generally a pyramidal texture size of substantially 2-4 microns, with said dissolved silicon having a concentration ranging from substantially 15 g/L to substantially 45 g/L; and
maintaining said aqueous solution at a temperature of between substantially 65 degree C to substantially 95 degree C.
7. A method according to claim 6, wherein said temperature is maintained between substantially 80 degree C to substantially 90 degree C.

8. A method according to claim 6 or 7, wherein said hydroxide is sodium or potassium hydroxide.
9. A method according to any one of claims 6-8, further comprising:
rinsing said silicon wafer in an aqueous solution of hydrochloric acid followed by rinsing it in deionised water.
10. A method according to any one of claims 6-9 is preceded by:
cleaning said silicon wafer in acetone followed by rinsing it in deionised water.
11. A method according to claim 10, wherein said cleaning in acetone is followed by cleaning in an alcohol.
12. A method according to claim 10 or 11, wherein said cleaning and rinsing are carried out in an ultrasonic cleaner.