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Highly-efficient low cost anisotropic wet etching of silicon wafers for solar cells application

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In this work, a novel aqueous etching solution was investigated for texturization of silicon substrates. Nearly 30% of incident light is reflected from the surface of crystalline silicon due to its high refractive index. Surface texturization is an efficient practice to reduce surface reflection by enhancing light trapping. Newly formulated etching solution was evaluated for optical reflection, surface morphology and hydrophilicity of silicon substrates. Amazingly, experimental results demonstrate lowest optical reflectance, improved surface morphology as well as enhanced periodicity of the resulting pyramids. A remarkably lowest surface reflectance of 9.94% was achieved. Meanwhile, addition of IPA in the solution plays a major part in improving hydrophilicity of the silicon substrates. https://doi.org/10.1063/1.5012125

I. INTRODUCTION

Silicon solar cells are most widely used to stream clean, renewable electrical power.[1] One of the most challenging errand in the silicon solar cell is minimizing the optical reflection, induced by the high refractive index of crystalline silicon (3.4).[2,3] The high optical reflection properties have been reduced by using antireflection coating (ARC),[4] it can also be achieved by texturing the front surface of silicon substrates by anisotropic wet etching.[5,6] Light trapping[7] can be explained by the Lambertian light trapping in textured solar cells, with the thermodynamic limit of maximum absorption in a slab whose thickness is much larger than the wavelength of light.[8–11] Pyramidal structure is a very efficient geometry that enables the light to randomly scattered, especially the light will be able to travel a much longer optical path, thus the optical absorption[12] is enhanced due to a prolonged light-matter interaction time.

Chemical anisotropic etching is a promising approach toward the low-cost solar cells with pyramidal surface structure. Recent etching processes usually employ alkaline etchants i.e. aqueous solutions of Potassium hydroxide (KOH),[13] Sodium Hydroxide (NaOH)[14] and isopropyl alcohol (IPA) as a surface additive.[15] These solutions are mostly chosen due to their low cost and less time consumption. However, these etching processes have some drawbacks such as poor surface morphology and irregular pyramid size.[16] Nevertheless, more advanced and sophisticated techniques are being used which assures to have enhanced performance. Yet most of these techniques still have high cost and

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the process itself is highly complicated. For instance, the standard procedure of forming structures require a high-cost step of depositing Si_3N_4 as hard mask with plasma-enhanced chemical vapor deposition (PECVD).[17] There have been also reporting of using some inventive etching solutions i.e. anhydrous sodium acetate (CH_3COONa) and tetramethyl-ammonium hydroxide (TMAH).[18]

In the current study, we developed a novel, simple and low-cost technique, employing potassium hydroxide (KOH), sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) all together in a specific concentration to achieve better results. Influence of experimental parameters such as KOH, NaOH and Na_2SiO_3 concentration, temperature of the etching solution during experimental process, effect of etching time on reflectance and surface morphology were studied and compared with other etching solutions. Moreover, the effect of IPA on the hydrophilicity was also examined.

II. METHODS AND EXPERIMENTS

We employed *n*-type Czochralski (CZ) Crystallographic structure <100> with an area of (20 mm x 20 mm) and thickness of 300 ± 10 μm. Prior to texturing silicon substrates were cleaned by RCA process.[19] The etching solution is prepared to have a constant temperature of 80 °C. Etching was then performed by immersion of silicon substrates into the etching solution for a specific period of time with a constant temperature. Afterward, the etched silicon substrates were immersed in the deionized water to wash out any residue of the etchant, followed by drying using pressurized nitrogen gas. Before texturization of KOH, NaOH and Na_2SiO_3 etchant solution, we performed number of experiments using different etching solutions to study their effect for comparison. The etchants we studied are aqueous solution of NaOH (5 wt%), KOH (8 wt%), Na_2SiO_3 (4 wt%) and KOH + NaOH + Na_2SiO_3 (2 wt% + 2 wt% + 1 wt%). Texturization result of the aqueous (KOH + NaOH + Na_2SiO_3) solution was found to be the best in all of the other etching solutions in terms of surface morphology, structure of pyramids and reflectance of the substrates. Texturing of silicon substrates was then performed by various concentration for different etching time and temperature varying between 75 °C ~ 85 °C.

The surface morphology, roughness and structure of the textured silicon substrates was investigated through Scanning Electron Microscope, SEM (X-Max, Zeiss, Ultra Plus, Gemini), Oxford Instruments Co. Ltd. The front surface optical reflectance was measured by using the IdeaOptics (PG2000-Pro EX) Scientific Class optical fiber Spectrometer. The AFM topographic images were perform by BRUKER, NanoScope® V & Nikon Multimode ScanAsyst and the contact angle of PEDOT:PSS with silicon substrates was measured by using a professional camera with macro lens (Nikon D5600).

III. RESULTS AND DISCUSSIONS

We choose the etching solution of KOH + NaOH + Na_2SiO_3 based on the initial experimental results which were performed earlier with optimized concentration of 2.5 wt% + 2.5 wt% + 2 wt%, respectively. The formula we developed is a step forward compared to other recipes by taking into account the etching dynamics. All these solutions were used to etch the silicon substrates at a temperature of 80 °C and for a time of 25 minutes.

We studied the surface morphology, hydrophilicity and measured optical reflectance of each sample etched by a different etching solution. Table I shows a comparison of the optical reflectance for silicon substrates etched by different etching solutions for time t = 25 minutes. The optical

TABLE I. Surface reflectance of silicon substrates etched by different etching solutions for 25 minutes.

Silicon Samples	Reflectance (%)
Planar silicon surface	31.03 ± 0.51
KOH	15.96 ± 0.88
NaOH	15.24 ± 0.67
Na_2SiO_3	13.25 ± 0.56
NaOH + KOH	12.12 ± 0.71
NaOH + KOH + Na_2SiO_3	09.94 ± 0.43

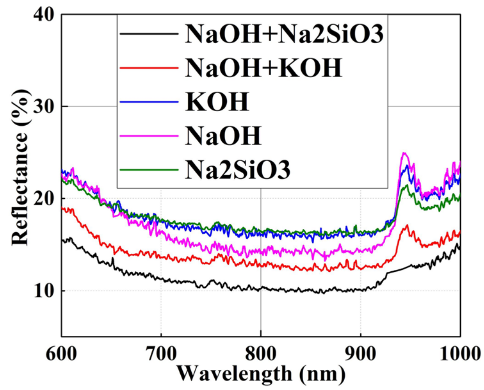

FIG. 1. Comparison of optical reflectance curves of silicon substrates textured by different etching solutions.

measurements demonstrate that texturization of Si substrates using aforementioned etching solution leads to a significant reduction in optical reflection. Typically, a single component etching solution results in 15% ~ 20% reduction in optical reflection. Interestingly, the KOH + NaOH + Na_2SiO_3 etching solution results in the lowest value of surface reflection.

The significantly reduced optical reflectance of silicon substrates can be attributed to the uniformity, surface morphology and periodic pyramidal structure. These results prove potential of KOH + NaOH + Na_2SiO_3 etching solution for texturization of silicon substrates. However, to avoid unfavorable charge trapping phenomenon due to shunt resistance R_{sh} fabrication of solar cell device with suitable substrate scales and physical tailoring method is required.[20] Figure 1 shows the optical reflectance of silicon substrates at a wavelength of 600 nm to 1000 nm showing lowest light reflectance in visible spectrum[21] as well as near infrared[22] (NIR) region. Low reflection at NIR will ensure photon absorption resulting in enhanced performance of the solar cell device.

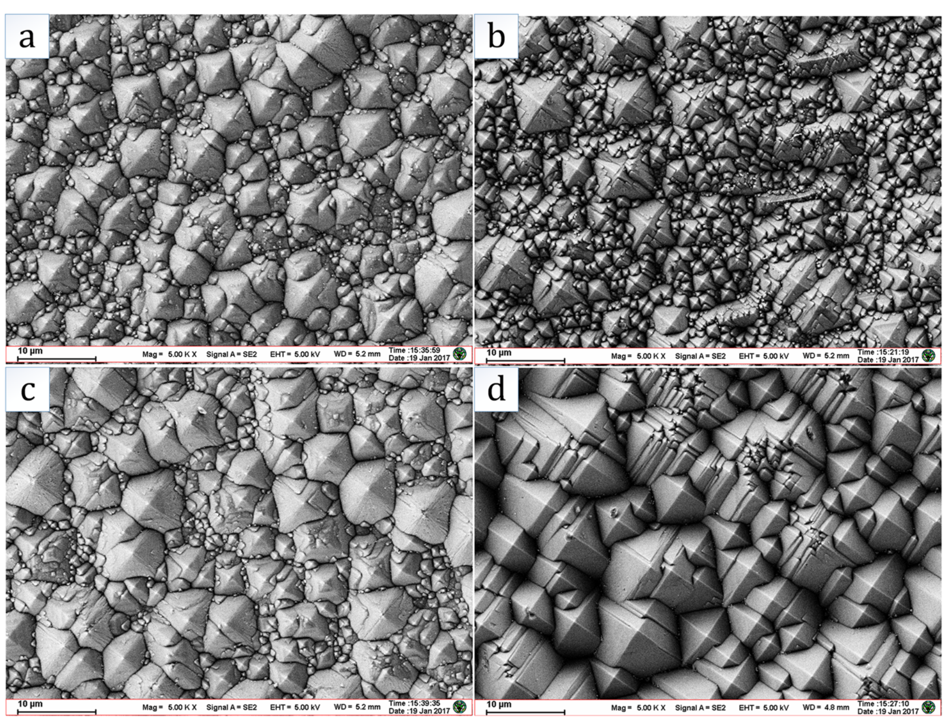

FIG. 2. SEM images of the silicon substrates textured by different etching solution (a) KOH, (b) NaOH, (c) Na_2SiO_3, (d) KOH + NaOH + Na_2SiO_3.

Surface morphology has a great effect on the optical absorption, performance of solar cell device and achieve higher efficiencies. Figures 2(a)–2(d) shows the SEM images of the silicon substrates etched by different etching solutions. It can be seen from Figure 2(a) substrate etched by KOH have larger free spaces (voids) between the pyramids and pyramids are not uniform as well as the valley between the hillocks are not completely textured. While in Figure 2(b) the substrate etched by NaOH which have completely covered the valleys between the hillocks but the periodicity is not satisfactory. Furthermore, Figure 2(c) shows the substrate etched by Na_2SiO_3 etching solution in which the pyramids are not uniform, voids can also be notice clearly. However, Figure 2(d) shows silicon substrate textured by the etching solution of KOH + NaOH + Na_2SiO_3 has improved surface morphology and periodicity of pyramids in comparison with the other etched substrates. Figure 3, illustrates the cross-sectional view of etched Si substrates, Figure 3(a) show substrate etched by KOH + NaOH + Na_2SiO_3, while that of figure 3(b) etched by KOH. These images demonstrate that the surface morphology of figure 3(a) is neat and clean, and most importantly the periodicity of the pyramids show significant enhancement which could not be realized in the substrate etched by KOH texturization solution 3(b). So, we can surely state that silicon substrate etched by the texturization solution of KOH + NaOH + Na_2SiO_3 improves the light absorption, surface morphology, uniformity and periodicity of the pyramids as well as reduce the reflectance effectively.

To further investigate surface roughness, we employ Atomic Force Microscopy to obtain the surface topography of the etched silicon substrate. Figure 4, shows the AFM micrograph of etched substrate. From the AFM image we have measured the average roughness "Ra" 221 nm and RMS "Rq" 281 nm indicating that the pyramids are uniform and periodic and no voids have been detected.

On the other hand, etching of silicon substrates also creates deformities in the textured surface as we already discussed and shown in Figures 2 and 3. However, it has been reported that IPA additive in the etching solution improves the hydrophilicity of silicon substrates as well as trim down

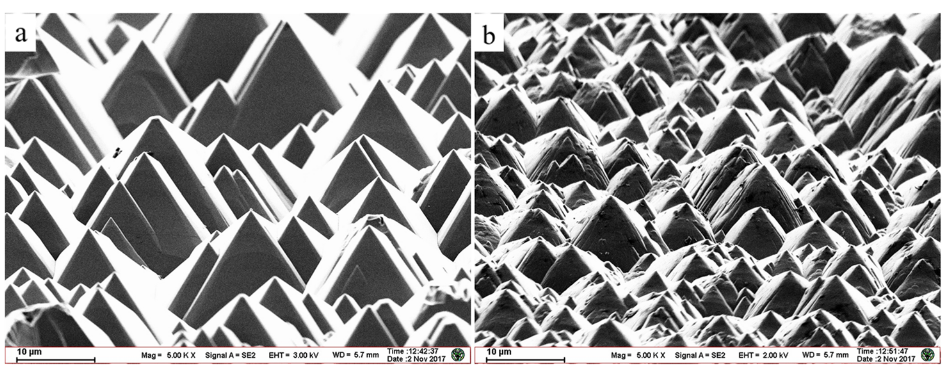

FIG. 3. Cross-sectional SEM images of etched silicon substrates (a) KOH + NaOH + Na_2SiO_3 (b) KOH.

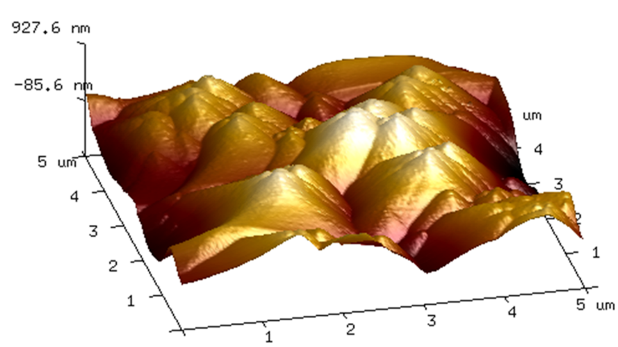

FIG. 4. AFM image of silicon substrate etched by KOH + NaOH + Na_2SiO_3.

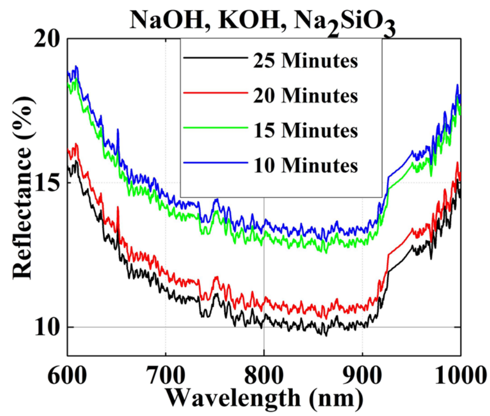

FIG. 5. Reflectance curves of silicon substrates textured by KOH + NaOH + Na_2SiO_3 etching solution at temperature, T = 80 °C and time, t = 10, 15, 20, 25 minutes.

the deformities in the surface morphology.[23] Hence, we use different concentration of IPA (2 wt%, 4 wt% 6 wt% and 8 wt%) in the etching solution. After employing IPA in the etching solution result demonstrates that reflectance of the front surface was decreased (from 10.15 % to 9.94 %) as described in Table I. However, increasing the concentration of IPA in etching solution increases the reflectance as well as time of etching reaction. However, to optimize the etching process of the newly developed etchant, a number of experiments have been carried out at temperature, T = 80 °C by varying the etching time i.e. 10 minutes, 15 minutes, 20 minutes and 25 minutes. We have found an obvious trend of decrease of optical reflection over the whole wavelength range when the etching time increases.

Figure 5 shows the differences between reflectance curves of various etching time and Table II, describe reflectance values of the textured silicon substrates etched for a different time, while using the same concentration of etching solution. Besides etchant recipe, the etching time is one of the most important parameters in a chemical reaction, as the etching dynamic requires adequate time to reach the equilibrium status. While commercially relatively short time is preferred to increase the production efficiency. As many factors involved in the R% of the c-Si substrate such as pyramid size, angle of pyramids, diameter of the pyramids, uniformity, periodicity, etching time, and optimized concentration of etchants. Therefore, a trade-off should be made to determine the most appropriate conditions for etching.

Surface energy is one of the most important property of solid materials, it can be measured by quantitative contact angle measurements. To investigate improvement in the hydrophilicity of silicon substrates, the PEDOT:PSS contact angle (θ) was measured for two different substrates. Shown in Figure 6(a) the contact angles (θ) for the silicon substrate etched by KOH + NaOH + Na_2SiO_3 without IPA additive and figure 6(b) show that of substrates etched by KOH + NaOH + Na_2SiO_3 with IPA are 50.5 ± 2° and 28.6 ± 1.8°, respectively. It is also reported that the surface topographic features could influence the angle of contact to some degree.[24,25]

Silicon substrates etched by KOH + NaOH + Na_2SiO_3 and IPA shows 43.37% reduction in the contact angle of PEDOT:PSS with the silicon substrate. The surprisingly enhanced wettability of Si substrates is referred to the treatment of IPA additive in the etching solution. IPA additive enhances dispersal of the PEDOT:PSS aqueous solution and resulting in complete coverage of Si substrate. It

TABLE II. Optical reflectance of silicon substrates textured for different etching time at temperature of 80 °C.

Etchant time KOH + NaOH + Na_2SiO_3	Reflectance (%)
10	14.97 ± 0.76
15	12.56 ± 0.88
20	10.28 ± 0.56
25	9.94 ± 0.43

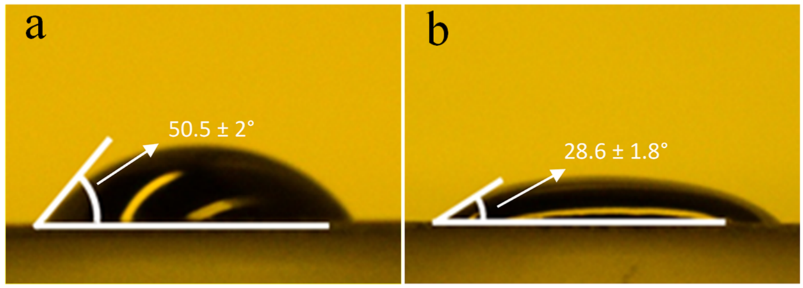

FIG. 6. Photographs of PEDOT:PSS drops on the silicon substrates after texturing with KOH + NaOH + Na_2SiO_3. (a) Textured without IPA additive. (b) Textured with IPA additive.

is beneficial in overcoming sheet defects of PEDOT:PSS, such as bubbles and microvoids that are created during spin coating course.[26]

IV. CONCLUSION

In conclusion, we perform texturization of silicon substrates employing newly developed etching solution which demonstrates better and improved results by reducing the optical reflectance as well as improving the surface morphology. Moreover, the IPA additive was effective in improving the hydrophilicity of the etched silicon substrates. This etching solution could be employed in commercial photovoltaic industry as well some application of MEMS to reduce cost, time consumption and improve etching results.

SUPPLEMENTARY MATERIAL

See supplementary material for includes graphical illustration of experimental steps, graph showing reflectance from (400 nm ~ 1000 nm) for different etchants used in study, effect of the pyramid structure on shunt pathways, absorption enhancement and effect of stirring and temperature on the process of etching.

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There is no conflict of interest to declare.

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