Surface Texturing for Silicon Solar Energy by Wet Acid

Kelvii Wei GUO

Department of Mechanical and Biomedical Engineering, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon Tong, Kowloon, Hong Kong

Abstract

To date, because of solar energy storage coupled with nanomaterials, surface engineering has become an essentially critical method for functional electrode design. Despite years of research on nanoscale materials for energy storage, commercial batteries still make use of microscale materials for electrodes. This is due to a combination of manufacturing challenges for nanoscale materials and the reactive nature of nanoscale materials that leads to high irreversible capacities associated with solid electrolyte interphase formation.

Surface texturing is a powerful tool to decouple bulk material properties from surface characteristics that often bottlenecks energy storage applications of nanomaterials and has been successfully used to improve the efficiency of photo detectors and solar cells due to a reduction in reflections at the surface. Therefore, the simple wet acid surface texturing methods for green energy-silicon solar energy are reviewed with the aim to provide the vital information about the growing field in surface engineering of solar energy with environmental friendly nature.

Keywords: Solar energy, Surface texturing, Green energy, Wet acid texturing, Alkali hydroxide etchants, Isopropyl alcohol (IPA), Tetramethyl ammonium hydroxide (TMAH) etchant, Silver etchants.

Introduction

Solar energy, as a popular green energy, is radiant light and heat from the Sun. The large magnitude of solar energy available makes it a highly appealing source of electricity. The International Energy Agency has said that solar energy can make considerable contributions to solving some of the most urgent problems the world now faces: The development of affordable, inexhaustible and clean solar energy technologies will have huge longer-term benefits. It will increase countries’ energy security through reliance on an indigenous, inexhaustible and mostly import-independent resource, enhance sustainability, reduce pollution, lower the costs of mitigating climate change, and keep fossil fuel prices lower than otherwise. These advantages are global. Hence, the additional costs of the incentives for early deployment should be considered learning investments; they must be wisely spent and need to be widely shared [1].

In a textured surface, rather than being lost, the reflected light can strike the silicon surface again to minimize reflection. Any “roughening” of the surface reduces reflection by increasing the chances of reflected light bouncing back onto the surface, rather than out to the surrounding air.

Principle of Texturing for Anti-reflection

Energy conversion efficiency is a critical consideration in the application of solar cells, especially for the silicon solar cells. Texturing has been used as a technique to improve the efficiency of photodetectors and solar cells due to a reduction in reflections at the front surface.

The anti-reflecting features may be cones, pyramids, pillars, and other features, and, when such features are used for diffusion and for the scattering of light may be distributed in a random fashion. It should be noted that any feature that produces the desired diffusive light scattering is one that closely approximates a Lambertian scattering surface at the desired wavelengths of radiation. Lambertian scattering is ideal diffuses cattering providing light distributed over the whole half sphere or solid angle of 2π steradians [2]. Manipulating the feature sizes, dimensions, etc. allows the light anti-reflecting and light diffusing region to be tunable for a specific wavelength. Varying the material near or deposited upon the anti-reflecting and light diffusing region can also be used to enhance these characteristics. Texturing will also change the absorption in the remaining part of the infrared and the visible light regions but this will not yet be considered. In the near infrared the index of refraction of silicon is n= 3.42 and the reflectance is about R= 30% from a single surface and transmittance through a single surface is T= 70% for normal incident waves. The absorption coefficient of silicon is very low in the near infrared. If there is no backside reflector radiation under normal incidence is reflected first from the first surface. There are successive reflections from both the back and internal reflections from the front surface resulting in a total transmittance, if there is no reflective layer or the oxide layer, of

\[
T_{\infty} = \left( \frac{TT}{(1+R^2+R^4+\ldots)} \right) = \frac{(TT)}{(1-R^2)}
\]

This result has been obtained using the sum of a geometric series. If both top and back surfaces are just polished silicon–air then this results in a total transmittance of 54% and a reflectance of 46%. The internal absorption, A, of infrared light where the absorption coefficient, α, is very low due multiple internal reflections in a sample of thickness, d, with a polished backside is

\[
A = \alpha d (1+R_2+R_2^2+\ldots) = \alpha d (1+R_2)/(1-R_2)
\]
The enhancement, $Enh$, in internal absorption by multiple internal reflections with a polished backside is

$$Enh = \frac{1 + R_2}{(1 - R_1 R_2)^2}$$

**Texturing Surfaces to Obtain an As-low-as-possible Reflectance**

The efficiency of a solar cell strongly depends on the interaction between the incoming light beam and the surface of the device. Any process enhances light-surface interaction increases absorption probability of the light; thus, improves generated current, in turn. Generated current could be improved either by light trapping or by increased device thickness. Considering fabrication costs and recombination losses, mechanically thin optically thick wafers are being focused on in terms of light trapping properties. Surface texturing among the other methods is an effective and more lasting technique in reducing reflections and improving light trapping.

It shows that fabricated solar cells with different patterns ended up with different device performance [3,4]. Amongst them, holes of 4 μm diameter and 5 μm gap showed a remarkable trend for varying hole depths. As plotted in Figure, increasing hole depth resulted in better cell performance.

**Wet Acid Texturing by Alkali Hydroxide Etchants**

Alkali Hydroxide Etchants + Isopropyl Alcohol (IPA)

There are two major losses that reduce the conversion efficiency of silicon solar cells: optical losses and electrical losses. Optical loss by surface reflection can be prevented by the use of an anti-reflection coating or by surface texturing. It is well known that polished wafers reflect 30% of the incident light. Reducing the extent of surface reflection can increase the short circuit current and thereby increase the conversion efficiency of the solar cell.

Texturing the surfaces of silicon wafer is one of the most important ways of increasing their efficiencies. The texturing process reduces the surface reflection loss through photon trapping, thereby increasing the short circuit current of the solar cell[5].

Nowadays different technologies of crystalline silicon (c-Si) solar cells, consisting in mono, poly, and multi c-Si, represent nearly 80% of the total world wide photovoltaic (PV) production. For wet texturing solutions consisting of potassium hydroxide (KOH) or sodium hydroxide (NaOH), combined with deionized water (DI H$_2$O) and isopropyl alcohol (IPA) were used to produce pyramid-like structures on c-Si surfaces with low reflectance values.

For c-Si solar cells the tendency is to reduce the amount of silicon, since this represents the main cost of the overall solar cell, therefore one direction followed is the research of the development of ultrathin c-Si wafers.

On the other hand, there is a constant research on how to improve the c-Si solar cells fabrication processes, with the aim to increases the conversion efficiency, the study of light trapping in the silicon surface has attracted much attention, since a reduction in the amount of light reflected form the solar cell surface, results on an increase of the short circuit current ($I_{sc}$) and therefore on the efficiency.

This issue has been partially solved using anti reflective coatings (ARC), as silicon oxide – SiO$_2$ [6], siliconnitride – SiN$_x$ [7] and sol-gel Al doped zinc oxide-AZO [8], among others. Some of those films have demonstrated excellent optical transmittance (~90%) in the 400-1100 nm wavelength range. As well, for HIT solar cells, transparent conductive oxides (TCOs) as indium tin oxide – ITO are widely used due to their very high transmission values (close to 90% in the range of 300-900 nm of the electromagnetic spectrum) and low resistivity [9].

Another way to increase the conversion efficiency is texturing the c-Si wafer surface with alkaline solutions; this technique has been widely studied and incorporated to industry, since the pyramid-like structures that are produced are very suitable to reduce the reflected light to values below 15%[10].

To date, the texturing of crystalline silicon is usually carried out using alkaline solutions. Such solutions resulted in anisotropic etching that leads to the formation of random pyramids. Before
the texturing process is carried out, saw-damage etching is performed in order to remove the surface defects and damage caused by wire sawing. In general, alkali hydroxide etchants potassium hydroxide (KOH) solution and sodium hydroxide (NaOH) are used for saw-damage etching. This etching results in a flat surface.

The major ion involved in the silicon etching process is the hydroxyl ion (OH\textsuperscript{-}), which attacks the silicon surface:

\[ \text{Si} + 2\text{OH}^- \rightarrow \text{Si(OH)}_2^{2-} + 4e^- (4) \]

Ions from the silicon crystal react with H\textsubscript{2}O in the solution. At the same time, the H\textsubscript{2}O dissociates and generates hydrogen gas:

\[ 4\text{H}_2 + 4e^- \rightarrow 4\text{H}_2\text{O} (5) \]
\[ 4\text{H}_2\text{O} \rightarrow 4\text{OH}^- + 2\text{H}_2 \]

The regenerated hydroxyl ions attack the neutral silicon again, thereby causing the reactions to continue.

Representative result of texturing for solar cell is forming random pyramids on the surface. Such pyramids are produced by anisotropic etching, which is caused by the difference in the densities of the planes in the (100) and (111) directions. Since the plane in the (111) direction is denser than that in the (100) direction, the etching rate in the (111) direction is much slower.

Isopropyl alcohol (IPA) is added in order to control the etching rate and thereby prevent an explosive reaction between the silicon surface and the OH\textsuperscript{-} ions. In general, as-cleaned wafers or wafers that have been saw-damage etched using an alkaline etchant are used for the fabrication of solar cells. The random pyramids formed on these wafers are typically 7-10 µm in size. Acidic etching of silicon is isotropic in nature and therefore results in the surface features to become “round” in shape.

Vazsonyi et al [11] took sodium hydroxide and isopropanol solutions texturing monocrystalline wafers and obtained the highest pyramid density on the silicon surface when the etching solution had a relatively high (0.6 µm/min) etch rate in the <100> direction with an anisotropy coefficient of 10, being the quotient of etch rates in the <100> and <111> crystallographic directions.

In 2009, Park et al [12] investigated surface texturing by saw-damage etching using the proposed acidic solution with the mono-crystalline boron-doped (100) silicon wafers with resistivities 6-12 Ωcm. The thickness of wafers was 270 µm. The surfaces of the wafers were first cleaned in order to eliminate any organic and metal impurities. Both a sulfuric acid mixed with hydrogen peroxide solution (SPM) and a hydrochloric acid mixed with hydrogen peroxide solution (HPM) were used for this cleaning process. After rinsing the wafers with sufficient de-ionized water (DIW) between each cleaning step, wafers were dipped in buffered oxide etching (BOE) solution in order to remove the native oxide layer. For comparison, wafers with three different surface morphologies were prepared. The chemical composition and process conditions are listed in Table.

Sample 1 was not saw-damage-etched wafer and Sample 2 was saw-damage etched with KOH solution. The final wafer was saw-damage etched with an aqueous acid mixture (Sample 3). All of the wafers were then anisotropically etched using solution mixture of KOH and IPA.

The surface of Sample 1 just after cleaning was very rough and had many defects and damaged areas. When such defects and damaged areas are allowed to remain, it is difficult to fabricate uniform and well-aligned solar cell. Moreover, the efficiency of the solar cell was decreased by increased surface recombination probability of the electrons and holes. For these reasons, defects and damaged areas are removed by saw-damage etching, normally using an alkaline etchant. KOH was used (Sample 2). During the etching process, the wafers were isotropically etched at a rate of 2 µm/min against the (100) direction. The etching clearly reduces the surface roughness. Square shapes (10 µm width, 5 µm high in average) were formed on the surface during the etching process. As time progressed, the squares become wider, thereby flattening the surface.

However, when using an acidic solution (Sample 3) to remove saw-damages, it remained round in shape on the surface. The mechanism of acidic saw-damage etching was shown below.

Oxidation

\[ 3\text{Si} + 4\text{HNO}_3 \rightarrow 3\text{SiO}_2 + 4\text{NO} + 2\text{H}_2\text{O} (7) \]

Removing Oxide

\[ 3\text{SiO}_2 + 18\text{HF} \rightarrow 3\text{H}_2\text{SiF}_6 + 6\text{H}_2\text{O} (8) \]

First, silicon oxidation occurs upon exposure to nitric acid. Then, hydrofluoric acid removes the oxidized layer, thereby forms H\textsubscript{2}SiF\textsubscript{6}. At the same time, acetic acid acts as a buffering agent that prevents nitric acid from decomposing into NO\textsubscript{3}\textsuperscript{-} or NO\textsubscript{2}\textsuperscript{-}.

Upon texturing, using a solution of KOH in IPA, random pyramids were formed on all of the different types of wafers. In the case of the just cleaned wafer (Sample 1), many defects remain on the surface after texturing. However, Samples 2 and 3 do not show these defects due to saw-damage etching. The pyramids of Sample 2 were 7-10 µm in size. By comparison, the pyramids of Sample 3 were just 3-4 µm in size. These results show that the surface condition before the texturing step affects the formation of the pyramids.

When round craters on the surface are formed by acidic saw-damage etching, there could be more exposure of (111) planes that have lower etching rate due to high density of plane and resistivity. It seems to act as a stable starting point for etching. Hence, reducing the size of the pyramids means that more pyramids can form on the same surface area.

Among the three solar cells, Sample 1 showed the lowest conversion efficiency. This can be caused by the many defects on its surface that increase series resistance. In contrast, Sample 3 showed the best cell characteristics. Compared to Sample 2,
Sample 3 has a similar open circuit voltage (Voc) and fill factor (FF) but a higher short circuit current (Jsc) of about 3.4 mA/cm². The increased Jsc indicates an improvement in the photogeneration. Therefore, this can explain that improved textured surface by acidic saw-damage etching contributes to enhance conversion efficiency by effective photon trapping evidenced by decreased reflectance and increased Jsc.

**Alkaline Etchants without Isopropyl Alcohol (IPA)**

Chu et al [13] proposed a simple and cost-effective approach for texturing crystalline silicon wafers without surfactant added in alkaline etchants.

The etching experiments were carried out using 300º, p-type, <100> oriented, crystalline silicon wafers with resistivity 1–3 Ωcm. Before texturization, the wafers were etched in 10% hydrofluoric acid (HF) to remove native oxide and rinsed in deionized water. The wafers were then etched in KOH (1 wt%) solutions at different temperatures for 10, 15, and 20 min. The etching solution was heated with a temperature-controlled hot plate. The hydrogen bubbles produced during etching were trapped on the wafer surfaces utilizing the stainless steel metal grids with different square openings with 1, 1.5, 2, and 3 mm square opening for texturing at 1 and 2 mm wafer-to-grid separations.

The pyramids fabricated using the proposed approach were dependent not only on the conditions of the KOH etchants but also on the structures of the metal grids to the silicon wafers. The silicon wafers were textured in the KOH solution at 90 ºC for 20 min using the metal grids with different sizes of openings. The separation between the wafers and the grids was kept at 1 mm (Since the typical diameter of the bubbles was around 2-3 mm. Therefore, the bubbles could not function as the etch mask effectively during the etching. The bubble trapping capability of the grid decreased if the wafer and the grid were further separated).

Without any antireflection coating, an average weighted reflectance of 15.1% is achieved. In addition to the fact that isopropyl alcohol (IPA) was no longer needed in the etching process, the cost of the raw materials used throughout the entire texturization (buffered-HF pre-treatment, KOH-only texturing and HCl/buffered-HF/DI-water post-treatment) of the proposed approach is 0.105 USD/wafer, a considerable reduction if compared with the cost of 0.154 USD/wafer in the conventional texturing process.

**TMAH Etchant+ Isopropyl Alcohol (IPA)**

Alkaline hydroxide etchants, as above-mentioned, such as potassium hydroxide (KOH) and sodium hydroxide (NaOH), have been widely used to texture crystalline silicon solar cells. However, these days, simple and quaternary ammonium hydroxide etchants, typically tetramethylammonium hydroxide (TMAH, (CH₃)₄NOH) (firstly proposed by Tabata et al in 1992 in order to make high-efficiency crystalline Si solar cells, the light reflection from the surface should be minimized and the formation of pyramidal surface of Si decreases the reflection substantially. To satisfy the requirement, alkaline-based anisotropic etchants (e.g. KOH, NaOH) have been widely used. However, as the alkaline-based solutions result in the mobile ion contamination to IC devices, a special effort has been made to develop new anisotropic etchants that do not introduce any mobile ions so that they can be IC fabrication compatible. Among these etchants, TMAH solution shows full compatibility with IC technologies, nontoxic, and good anisotropic etching characteristics. Compared to alkaline-based etchants, TMAH is readily controllable and its etch rate is constant over long etch times [14].) is used instead of KOH and NaOH due to problems associated with metal ion contamination.

Kim et al [15] investigated how the wet chemical etching process to form random pyramids was affected by surface conditions.

The p-type (100) mono-crystalline silicon wafers with a resistivity of 0.5–3.0 Ωcm and thickness of 200 µm was used. To witness the texturing behavior, three different surface wafers were prepared, namely saw-damage etched (SDE), polished, and as-cut wafers. The saw-damage etching process was performed with potassium hydroxide (KOH) for 10 min, at 80 ºC. The polished wafer was prepared by using chemical mechanical polishing (CMP).

After preparing the different surface wafers, the texturing process was carried out using a 20 wt% tetra-methylammonium hydroxide (TMAH) solution with isopropyl alcohol (IPA) at 80 ºC. Analysis of the process was performed after 2, 5, 10, 20, 30, and 60 min.

Results show that after 30 min of texturing time, the SDE sample is completely covered by pyramids. On the other hand, the as-cut and polished samples take more than 60 min to be covered. Surface texturing is an anisotropic wet-chemical etching technique that is commonly used to form random pyramids by utilizing differences in etching rates for the planes in the (100) and (111) direction [11]. The saw-damage etching process carries out isotropic wet-chemical etching to eliminate micro-cracks caused by the use of a strong alkaline solution (e.g., KOH) for wire sawing. However, this process creates squares and inclined planes due to incomplete isotropic etching, where the inclined plane is rough with no flat character.

For the SDE sample, it shows that pyramids are preferentially created in an inclined plane of squares that are generated through the saw-damage etching process. Because (111) planes are exposed by the inclined plane of squares, the SDE sample takes less texturing time than do the other sample types.

For the polished sample, pyramids are randomly created. The etching rate of the polished wafer is similar to any other defect-free surface; however, the as-cut sample was completely covered by secondary pyramids that were created after the first set of pyramids.

The etching reaction exhibited on the as-cut wafer is active due to the inherent surface defects, and for up to 10 min, many defects remain on the surface after texturing. After 20 min, the surface morphology does not indicate these defects, instead of the squares created by the saw-damage etching process since similar surface shapes were observed. During the texturing process of the as-cut wafer, texturing pyramids are created and surface defects are removed simultaneously.

As a result, texturing the surface of a silicon wafer brings about a reduction in the surface reflectance. The weighted reflectance of each sample is 11.0, 13.8, and 23.1% in SDE, polished, and as-cut wafer, respectively. However, each sample exhibits an almost equivalent reflectance after 60 min of texturing process time, where the reflectance is 10.7, 10.9, and 11.0%.
Silver Etchants for Nanoscale Texturing

Silver Etchants + Alkali Hydroxide Etchant

Lee et al [16] proposed a process called electro-less etching to investigate the density and size of silicon nanowires on a pyramid-textured silicon surface and its photovoltaic performance, especially on the minority-carrier recombination lifetime of silicon nanowires, and photovoltaic performance on the density and size of silicon nanowires on the pyramid-textured silicon surface.

The as-cut (1 × 1 cm²) p-type silicon wafers with a resistivity of 1–3 Ωcm and a thickness of 200 µm were etched by using 2 wt% potassium hydroxide (KOH) solution to produce randomly distributed square-based pyramids on the silicon surface and to remove sawing damage. The pyramid-textured silicon wafers were dipped into the mixture solution of AgNO₃ (0.068 g), deionized water (160 ml), and hydrofluoric acid (46 ml) for 30 s to deposit Ag nanoparticle masks on the pyramid-textured silicon surface. Then, the pyramid-textured silicon wafers with Ag nanoparticle masks were etched with a mixture solution of FeNO₃ (8.16 g), hydrofluoric acid (HF:46 ml), and deionized water (160 ml) for 0, 1, 2, 3, 4, 5, 7, 10, and 15 min, to produce silicon nanowires on the wafer surface.

Selective alkaline etching using KOH produced uniformly distributed square-based silicon (111) pyramids. Deposition of Ag nanoparticles using the mixture solution of AgNO₃, deionized water, and hydrofluoric acid for 30 s followed by electro-less etching using the mixture solution of FeNO₃, hydrofluoric acid, and deionized water for 1 min produced silicon nanowires 56 µm in diameter and 211 µm in height on the pyramid-textured silicon surface. The diameter of silicon nanowires on the pyramid-textured silicon surface increased initially up to ~56 nm when the electro-less etching time increased up to 2 min, and then maintained with ~109 nm although the electro-less etching increased further. Otherwise, the height of silicon nanowires on the pyramid-textured silicon surface increased from ~211 nm to ~1175 nm when the electro-less etching time increased from 1 min to 15 min. In particular, silicon nanowires tended to collapse with electro-less etching times that exceeded 10 min.

Results indicate that silicon nanowires on a pyramid-textured silicon surface probably enhance power conversion efficiency (PCE) by weakening the dependence of the light incident angle on PCE.

It illustrates that the silicon nanowire fabrication method using the Ag nanoparticle mask and electro-less etching is expected to be a key engineering technique that makes it possible to achieve maximum photovoltaic performance of solar silicon cells. Note that the p-type silicon photovoltaic cell with silicon nanowires on [111] pyramid-textured silicon surface enhanced ~10% in PCE compared to a conventional p-type silicon photo-voltaic cell that skipped anti-reflective coating process (plasma enhanced chemical vapor deposition). In addition, the process cost of the deposition of Ag nanoparticle mask and electro-less etching is probably similar or cheaper than that of anti-reflective coating process.

Silver Etchants without Alkali Hydroxide Etchant

Srivastava et al [17] reported a simple and fast etching process yet effective for nano-scale texturing of mc-Si surface using silver assisted wet chemical etching.

As-cut (1-2 Ωcm, B-doped) p-type mc-Si wafer of thickness ~250 µm and 100 × 100 mm² size are used as the starting material. Samples of 50 mm diameter are diced from the large mc-silicon wafers in order to have the identical electrical/electronic properties. The samples are first cleaned and etched in an HNO₃:HF:CH₃COOH = 5:1:1(v/v) etching solution to remove the saw damages. Thereafter, the samples are chemically polished (CP) in HF and HNO₃, solution at ~4 °C.

Three steps were taken: (i) deposition of a thin Ag layer onto the polished mc-Si using electro-less metal deposition in an aqueous 4 M HF solution containing 8 mM AgNO₃ (for 10 s); (ii) etching of the Ag deposited samples in H₂O₂:HF:H₂O₃:10:2:1 (v/v) solution at room temperature for 0–180 s; and (iii) removal of residual Ag particles from the samples in NH₄OH + H₂O₂ solution. Finally, the mc-Si samples are rinsed in deionized water and blown dry with nitrogen.

The surface of the etched samples are black in appearance for etch duration. It shows that 20 s < t_{etch} < 45 s; even under illumination at angles away from normal to the surfaces. For t_{etch} > 45 s surface is brownish. Results show that the nano-textured mc-Si surface with reflectance <5% enhances the photocurrent by ~20% in the short circuit current.

Knowledge Gap

Understanding the final wastes of wet acidic texturing is a critical issue to environmental pollutions. Unfortunately, it is still an area where a huge knowledge gap exists. The fate of final wastes and the resulting implications for environments-such as contaminated earth, pipelines, crops, under water, etc. are not well understood. The wider use of etchants in wet acidic texturing has increased their release into the environment through soil, water, and air, which may lead to unintended contamination of terrestrial and aquatic ecosystems.

The present state of knowledge in treatment with wastes of wet acidic texturing is still in a foundational stage along with silicon solar cell with nanostructures. Not only is data limited and inconclusive regarding texturing wastes’ and nano-silicon structures distributed in solar cells’ impacts in our daily life, but more information is needed on properties that control their effects in environments. Moreover, the interplay of these factors gives confounding results making it almost impossible to predict. Therefore, the difference between the potential benefits and harms of wet acid texturing is quite subtle and a large knowledge gap exists on the long-term impacts to the environment, especially on the human health.

Conclusion

For solar energy wet acid surface texturing is a powerful effective tool. Without any antireflection coating, the reflectance of etched surface can be achieved at about 10%. With the assistance of silver etchants, a more effective surface with nanostructures on mc-Si surface with the attractive reflectance <5% can be attained successfully. It illustrates that as a method for surface texturing, wet chemical etching is easy to operate besides its efficiency and cost. However, the fate of wet acidic texturing is a critical issue to environmental pollutions. The large knowledge gap between the potential benefits and harms of wet acid texturing is quite subtle and the final implications of wet acid texturing for environments must be thoroughly investigated.
Acknowledgements

The work is supported by the Strategic Research Grant (SRG) from City University of Hong Kong (Grant No.: 7004598).

References