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Improvement of screen-printed textured monocrystalline silicon solar cell performance by metal-assisted chemical etching

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Abstract

In this work, we investigate the potential use of stain etched porous silicon as one possible way to increase the silicon solar cell efficiency at low cost. A very simple method for the formation of porous silicon antireflection coatings on random pyramid textured screen-printed monocrystalline silicon solar cells is described. The process is based on electroless metal-assisted chemical etching by immersion of the fully processed cell in HF-H\textsubscript{2}O\textsubscript{2}-Ethanol without masking the contacts. Characterization of the porous silicon layer using SEM, EDX and UV-VIS-NIR spectrophotometry revealed that silver nanoparticles that are dissolved from the unmasked front grid contact by the HF acid greatly enhance the dissolution rate and therefore serve as catalysts for the porous silicon etching. The solar cell weighted reflectance was reduced from 45.08\% to 22.01\% after texturization and dropped further to 11.34\% after porous silicon formation under optimized conditions. The porous silicon antireflection layer led to a relative improvement of 24.64\% in the short-circuit current density with out fill factor deterioration. The open-circuit voltage increased by \textasciitilde7 mV and the cell efficiency was raised by 2.3\% absolute. The simplicity of the process makes it attractive for the cost-effective production of silicon solar cells.

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Keywords: metal-assisted chemical etching; porous silicon; silicon solar cells; antireflection

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1. Introduction

A well-established process step in the mass production of silicon solar cells based on (100) monocrystalline wafers is anisotropic texturization of the surface to reduce the average reflection from over 35% to about 11% [1]. In this process, etching in a hot KOH (or NaOH)-IPA-H2O solution leads to the formation of randomly distributed micro-pyramids on the wafer surface [2, 3]. The application of an antireflection coating (ARC) on the textured surface reduces the reflectance further to ~ 3% [1]. Most photovoltaic cell manufacturers apply a silicon nitride (SiNx) ARC using plasma enhanced chemical vapor deposition (PECVD). The disadvantages of this technique are the high cost of the plasma reactor and safety hazards associated with the precursor gas silane. A safer and cheaper alternative is the formation of a layer of porous silicon (PS) ARC.

Porous silicon has stirred great scientific and technological interest because of its use in a very wide variety of applications [4-6]. In particular, this material is very promising for application to silicon solar cells [7, 8], due to its unique combination of light trapping, antireflection property and light conversion ability [9, 10].

Among the many methods of PS preparation, the most popular for photovoltaic devices are electrochemical etching or chemical etching (also called stain etching) in HF-based solutions (for a comprehensive review see [11]). However, the complexity of the setup in the anodic dissolution process is an obstacle to large scale implementation. In contrast, chemical etching in diluted HF-HNO3-based solutions is a simple low-cost process which does not require external contacts and power sources. Several investigators have shown the benefit of PS layer formation on randomly textured silicon solar cells using electrochemical etching [12, 13] or stain etching with [14, 15] or without [16, 17] contact protection.

Recently, several groups of researchers have used metal-assisted electroless etching in HF-H2O2-H2O or HF-H2O2-Ethanol to form PS on pyramidally-textured monocrystalline silicon solar cells [18-22]. The metal-assisted etching was performed as a first step during solar cell fabrication after surface texturization, i.e. prior to emitter diffusion. In this process, Au [18-20] or Ag [21, 22] nanoparticles are first deposited on the silicon surface by electroless plating [12, 13], e-beam evaporation [18], the silver mirror reaction [22] or the Silvert method [21]. Then, etching in HF-H2O2-based solutions leads to the catalytic reduction of H2O2 on the metal, providing the holes which subsequently take part in the oxidation and dissolution of the silicon surface. A very promising cost-saving alternative approach which avoids completely the deposition of metal nanoparticles and uses instead the screen-printed front Ag grid contact of fully metallized planar multicrystalline silicon solar cells as a catalyst has been proposed by Tsujino et al. [23]. These authors reported that PS layer formation in HF-H2O2 was enhanced by the presence of the contact, reducing the reflectivity to ~ 20% after a 10 second etch. Motivated by this result and the simplicity of the method, our group demonstrated a substantial boost of 3% (absolute) in the efficiency of planar polished screen-printed monocrystalline silicon solar cells after etching in HF-H2O2-Ethanol [24]. It was shown that silver nanoparticles that are detached from the front grid contact act as catalytic sites for PS layer formation. In this paper we successfully apply this process to randomly textured monocrystalline silicon solar cells.

2. Experimental

As starting material we used 4-inch diameter as-cut, solar-grade, Cz-grown, (100) oriented, p-type (boron doped) silicon wafers with a resistivity of 0.5-3 Ω.cm and a thickness of 450 μm. The saw damage was first removed in a hot NaOH solution. Random pyramid surface texturization was carried out using a 1 wt.% aqueous KOH solution with 5 vol.% isopropanol at 70°C for 20 minutes. This was followed by cleaning in HCl and a final dip in dilute HF prior to the diffusion process. A heavily doped n+ emitter was
realized by diffusion at 920°C using a liquid POCl₃ source, leading to a sheet resistance of 22 Ω/Sq. Following diffusion, the phosphorous silicate glass was etched off in dilute HF and the parasitic junction at the edge was removed in a barrel dry plasma etcher. The wafers were then cut into ¼ wafers which were metallized by screen-printing and firing in an infrared belt furnace, of an Ag grid contact on the front side and a full Ag/Al contact on the back side. The total cell area was ~20 cm². Formation of the porous layer was accomplished by dipping the finished solar cells in a HF (48 wt.%) - H₂O₂ (30 wt.%) - Ethanol mixture at room temperature without any protection to the metal contacts. The solar cell process sequence is shown in Table 1. The total hemispherical reflectance was measured before and after porous silicon formation between 300 and 1200 nm at 1 nm intervals using a Varian Cary 500 UV-VIS-NIR spectrophotometer equipped with an integrating sphere. The reflectance curves include the reflectance of the screen-printed fingers of the metal grid but not the busbar. The weighted reflectance, R_w, was calculated by normalizing the reflectance spectrum to the photon flux of the AM1.5G spectral distribution in the 400-1100 nm wavelength range. The photovoltaic characteristics of the solar cells were obtained from illuminated I-V measurements using a solar simulator under standard conditions (AM1.5G, 100 mW/cm²). A Philips XL30 ESEM-FEG scanning electron microscope (SEM) with an X-ray energy dispersive detection system (EDX) was used for morphology observation and elemental analysis of the porous solar cell surface.

Table 1. Solar cell processing sequence

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Saw damage removal and cleaning</td>
</tr>
<tr>
<td>2</td>
<td>Random pyramid surface texturization</td>
</tr>
<tr>
<td>3</td>
<td>Heavy POCl₃ emitter diffusion</td>
</tr>
<tr>
<td>4</td>
<td>Diffusion glass removal</td>
</tr>
<tr>
<td>5</td>
<td>Parasitic edge junction isolation by plasma etching</td>
</tr>
<tr>
<td>6</td>
<td>Dicing the 4” wafers into ~20 cm² area samples</td>
</tr>
<tr>
<td>7</td>
<td>Screen-printed metallization and firing</td>
</tr>
<tr>
<td>8</td>
<td>Chemical etching for porous silicon formation</td>
</tr>
</tbody>
</table>

3. Results and discussion

As reported in our previous study [24], the solution composition and etching time are crucial parameters that control the partial dissolution of the front electrode, producing silver nanoparticles which then act as catalytic sites for PS layer formation. The solution composition was optimized and it was shown that the etching time must not exceed 10 seconds in order to avoid contact degradation. Here we apply the process to a textured silicon surface which is covered with straight square pyramids of height about 1-2 μm. Fig.1 shows a top view SEM micrograph of a porous film formed on a textured silicon solar cell which exhibits a large distribution of nanoparticles on the surface. The EDX analysis, shown in Fig.2, confirms that the particles are silver and therefore their detachment from the front contact grid. The silicon and oxygen peaks originate from the oxidized silicon area surrounding the nanoparticle. The PS layer is made of micropores which can clearly be seen on all pyramid facets (Fig.3) with a typical pore size in the range 15-80 nm. The cross-sectional SEM image of Fig.4 indicates that the porous layer thickness is between 200 and 250 nm and that craters with a diameter of ~400 nm are also present on the pyramids.
Fig. 1. SEM micrograph of PS layer formed on a textured monocrystalline silicon solar cell showing the presence of silver nanoparticles.

Fig. 2. EDX spectrum of a silver nanoparticle.

Fig. 3. SEM micrograph showing micropores on pyramid facets.

Fig. 4. SEM cross-sectional view of the porous layer covering the pyramidal structures. Craters with a diameter of ~400 nm can be seen.

Fig. 5 (a-d) illustrates the relative changes in the electrical solar cell parameters, short-circuit current density ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor (FF) and efficiency ($\eta$), as a function of etching time from 5 to 10 seconds. In addition to these parameters, the saturation current ($J_0$), ideality factor (n), series resistance ($R_s$) and shunt resistance ($R_{sh}$) were also extracted from the illuminated I-V curve using the analytical method of Saleem and Karmalkar [25]. Fig. 5(a) shows that $J_{sc}$ increases with the etching duration, as expected since more Ag particles are dissolved from the front grid contact as time evolves. The initial enhancement in FF observed after a 5 second etch (Fig. 5(b)) is attributed to thinning of the glass layer at the Ag grid-silicon interface by the HF contained in the solution, thus reducing the contact resistance [26]. Etching for longer times has a detrimental effect on FF, particularly after 10 seconds, due to contact deterioration by the HF acid. Fig. 5(c) shows the variation of both $V_{oc}$ and $J_0$ with etching time.
There is a good correlation between the variation of $V_{oc}$ and $J_0$. $V_{oc}$ is slightly improved upon etching for 5 or 7 seconds. This is due to the increase in $J_{sc}$ as can be calculated from the following relation (assuming an ideal diode):

$$V_{oc} = \frac{n k T}{q} \ln \left( 1 + \frac{J_{sc}}{J_0} \right)$$

$k$ is the Boltzmann’s constant, $T$ the temperature in degree Kelvin and $q$ the electronic charge. The calculation of $V_{oc}$ after 5, 7 and 10 second etching times gives 581.25 mV, 583.55 mV and 555.11 mV respectively. These values are very close to the corresponding measured values of 582.3 mV, 585 mV and 556.4 mV. Clearly, the cell treated for 10 seconds leads to a sharp $V_{oc}$ drop which is caused by the large increase in $J_0$ (~162 nA.cm$^2$ compared to 2.31 nA.cm$^2$ after a 7 second etch) which in turn is attributed to increased recombination of the greatly enlarged porous silicon surface area.

Fig.5(d) shows that the best increase in efficiency is obtained after 7 seconds of etching. The corresponding electrical cell parameters are given in Table 2. Fig.6 compares the total reflectance of the textured surface before and after porous etching for the optimal time of 7 seconds. The weighted reflectance decreases from 22.01% to 11.34%.

Fig.5 Relative changes of (a) short-circuit current density, (b) fill factor, (c) open circuit-voltage and saturation current and (d) efficiency as a function of etching time. The lines are guides to the eye.
Table 2. Results of light I-V measurements on a ~ 20 cm² textured silicon solar cell before and after PS ARC formation for 7 sec.

<table>
<thead>
<tr>
<th></th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
<th>$J_0$ (nA.cm²)</th>
<th>$n$</th>
<th>$R_s$ (Ω.cm²)</th>
<th>$R_{sh}$ (kΩ.cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Textured</td>
<td>577.8</td>
<td>20.30</td>
<td>71.3</td>
<td>8.4</td>
<td>1.20</td>
<td>1.35</td>
<td>0.55</td>
<td>1.50</td>
</tr>
<tr>
<td>Textured + PS</td>
<td>585.0</td>
<td>25.30</td>
<td>71.9</td>
<td>10.7</td>
<td>2.31</td>
<td>1.40</td>
<td>0.46</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Fig. 6 Total reflectance spectra of a textured monocrystalline silicon solar cell before and after formation of an optimal PS ARC in HF-H₂O₂-Ethanol for 7 seconds.

4. Conclusion

Metal-assisted etching in HF-H₂O₂-Ethanol has been applied to generate a PS ARC on textured monocrystalline silicon solar cells. In this method, silver nanoparticles dissolved from the front grid contact act as catalysts. A short dip of 7 sec was found sufficient to increase the photocurrent by ~25% (relative) and the energy conversion by 2.3% (absolute) without contact deterioration. The technique may prove to be a facile, lower-cost, viable alternative to the conventional stain etching in HF-HNO₃-based solutions for the reduction of solar cell reflectance losses.

Acknowledgements

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References


