ABSTRACT

Multicrystalline Si (mc-Si) cells have not benefited from the cost-effective wet-chemical texturing processes that reduce front surface reflectance on single-crystal wafers. We developed a maskless plasma texturing technique for mc-Si cells using Reactive Ion Etching (RIE) that results in much higher cell performance than that of standard untextured cells. Elimination of plasma damage has been achieved while reducing front reflectance to extremely low levels. Internal quantum efficiencies higher than those on planar and wet-textured cells have been obtained, boosting cell currents and efficiencies by up to 11% on monocrystalline Si and 2.5% on multicrystalline Si cells.

EXPERIMENTAL PROCEDURE

We developed several metal-catalyst assisted RIE-texturing techniques using SF6/O2 plasma chemistry in a Plasma-Therm 790 reactor. The cathode in the plasma chamber is constructed from graphite while the chamber walls and anode are made of aluminum. A large parameter space of power, pressure, gas ratio, flow rate, and etch time was investigated. A parameter range was found to be useful for texturing Si wafers up to 6" in diameter and mc-Si wafers of 130 cm². The textured surface exhibits a spectral reflectance between 1 and 5% for wavelengths below 1 μm without the benefit of anti-reflection films as shown in Fig. 1.

INTRODUCTION

The quality of lower cost multicrystalline-silicon (mc-Si) has increased to the point that its cell performance is close to that of single c-Si cells, with the major difference resulting from the inability to texture mc-Si affordably. This has reduced the cost-per-watt advantage of mc-Si. A low-cost, large-area, random, maskless texturing scheme independent of crystal orientation is expected to significantly impact the cost and performance of mc-Si photovoltaic technology.

Surface texturing for enhanced absorption in Si has been historically obtained by creating randomly distributed pyramids using anisotropic wet etchants, but this works well only on single-crystalline silicon because of its (100) crystallographic orientation. Various other forms of surface texturing have been applied to mc-Si in research, including laser-structuring, mechanical grinding, porous-Si etching, and photolithographically defined etching. However, these generally slow techniques may be too costly to ever be used in large scale production.

A Japanese firm has reported the development of an RIE-texturing process using Cl₂ gas, which textures multiple wafers per batch, making it attractive for mass-production [1]. Using this process, they have produced a 17.1% efficient 225-cm² mc-Si cell, which is the highest efficiency mc-Si cell of its size ever reported. This shows that RIE texturing can be done without causing performance-limiting damage to Si cells. In this paper, we will discuss an RIE-texturing process that avoids the use of toxic and corrosive Cl₂ gas.

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EXPERIMENTAL RESULTS

The challenge involved in incorporating the low-reflectance surfaces obtained from RIE-texturing into a complete solar cell has been to remove the plasma-induced contamination and surface damage without removing too much of the texture. Figure 2 shows the importance of removing all surface contamination before cells undergo phosphorus emitter diffusion.

The IQE of the textured region of the cell in Fig. 2b is still lower than that of the planar region even after RCA cleaning, probably due to residual surface damage. Fig. 3 shows results of the use of a damage removal etch (DRE) consisting of either KOH or nitric/HF to remove this damaged region.

With the selection of the proper DRE and RIE-texture processes, we were able to fabricate cells on monocrystalline Si whose IQE was increased to levels as high as that of our best wet-textured cells with reflectances almost as low. The results obtained using an Al-assisted RIE process are shown in Figure 4.
The cells in Fig. 4 were textured using a process that involved introducing tiny amounts of Al to the SF\textsubscript{6}/O\textsubscript{2} plasma. We later developed a different process in which the RIE chamber was pre-conditioned with other metal catalysts, allowing wafers to be textured one after another without having to add metal catalysts each time. Cell results using this process are shown in Figure 5.

The superior red-response of the RIE-textured cell shows that no degradation of the bulk diffusion length occurred, even though the metal-assisted texturing was done before the high-temperature diffusion step. This is due to the very thorough RCA cleaning that is done after RIE-texturing. The slight enhancement of RIE-textured red-response may be due to the sub-micron dimensions of the RIE-textured features, which act to diffract some of the incident light into the Si at large angles, promoting better current collection.

The combination of good blue response and low reflectance of the RIE-textured cell shows that all RIE-induced surface damage could be removed while retaining the surface morphology necessary for good absorption. The reflectance obtained with the conditioned texture appears to be even lower than that of the Al-assisted texture, with a AM1.5G spectrum-weighted reflectance of 5.6% that includes reflectance from the gridlines.

These two promising RIE-texture processes were each applied to groups of 12 mc-Si wafers from BP Solarex, and compared with another 12 planar control wafers from the same ingot. Then all wafers were processed through the Solarex cell production line using standard industrial process schedules. The cell performance results are shown below.

Table 2. Average ± standard deviation of IV parameters for 3 groups of 130-cm\textsuperscript{2} mc-Si cells processed at Solarex. Average $V_{OC}$ values were $578 \pm 1$ mV for all 3 groups.

<table>
<thead>
<tr>
<th>Cell surface</th>
<th>Efficiency [%]</th>
<th>$J_{SC}$ [mA/cm$^2$]</th>
<th>$V_{OC}$ [mV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Planar</td>
<td>12.0 ± 0.2</td>
<td>28.3 ± 0.1</td>
<td>0.73 ± 0.01</td>
</tr>
<tr>
<td>Al-assisted</td>
<td>12.1 ± 0.4</td>
<td>28.6 ± 0.3</td>
<td>0.73 ± 0.02</td>
</tr>
<tr>
<td>Conditioned</td>
<td>12.3 ± 0.4</td>
<td>28.6 ± 0.2</td>
<td>0.74 ± 0.02</td>
</tr>
</tbody>
</table>

Figure 4. Graphs a-c show comparisons of IQE, EQE, and hemispherical reflectance of RIE- and wet-textured mono-Si cells, and d shows the RIE/wet ratios of EQE and IQE curves. Because the EQE of the RIE-textured cell exceeds or almost matches that of the wet-textured cell, the $J_{SC}$ of an RIE-textured cell should match that of the wet-textured cell, and exceed that of a planar cell.

Table 1. Avg. illuminated IV parameters of mono-Si cells.

<table>
<thead>
<tr>
<th>Cell surface</th>
<th>Efficiency [%]</th>
<th>$J_{SC}$ [mA/cm$^2$]</th>
<th>$V_{OC}$ [mV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Planar</td>
<td>14.8</td>
<td>31.0</td>
<td>615</td>
</tr>
<tr>
<td>Wet Textured</td>
<td>16.0</td>
<td>34.0</td>
<td>612</td>
</tr>
<tr>
<td>RIE Textured</td>
<td>16.5</td>
<td>34.2</td>
<td>618</td>
</tr>
</tbody>
</table>
The average efficiency of the cells with conditioned texture increased 2.5% relative to the planar value due primarily to the higher cell currents. Fig. 6 shows reflectance and IQE data for median cells from each of the 3 groups.

The IQEs of the textured cells both show improved red-response due to the oblique light coupling into the Si, especially using the conditioned texture process. The slightly lower blue response is more than compensated for by the lower reflectance at short wavelengths. Both the textured cells show lower reflectance than the planar cell, but not as low as was obtained on mono-Si. This is because a longer-duration nitric/HF DRE was used on these cells to ensure complete damage removal, and this resulted in loss of some of the texture. Cells are now being fabricated with less aggressive DREs that should have lower reflectance and higher performance.

DISCUSSION

One of the advantages of the metal-catalyzed texture process is the ability to obtain different feature shapes and sizes while retaining a wide process parameter window for repeatability. This is shown in Figure 7.

These different morphologies vary the amount of oblique light coupling, resulting in the different textured red-responses of Fig. 6, even though the reflectances were similar.

CONCLUSIONS

A plasma process using metal catalysts and non-corrosive etch gases was developed to texture mc-Si cells, resulting in higher currents and efficiencies.

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REFERENCES