ABSTRACT

We developed a self-aligned emitter etchback technique that requires only a single emitter diffusion and no alignments to form self-aligned, patterned-emitter profiles. Standard, commercial, screen-printed gridlines mask a plasma-etchback of the emitter. A subsequent PECVD-nitride deposition provides good surface and bulk passivation and an antireflection coating. We succeeded in finding a set of parameters which resulted in good emitter uniformity and improved cell performance. We used full-size multicrystalline silicon (mc-Si) cells processed in a commercial production line and performed a statistically designed, multiparameter experiment to optimize the use of a hydrogenation treatment to increase performance. Our initial results found a statistically significant improvement of half an absolute percentage point in cell efficiency when the self-aligned emitter etchback was combined with a 3-step PECVD-nitride surface passivation and hydrogenation treatment.

INTRODUCTION

The use of plasma-enhanced chemical vapor deposition (PECVD) of silicon-nitride as a low-temperature surface passivation technique for silicon solar cells is now widely recognized as a method for providing surface passivation and an effective antireflection coating (ARC) at the same time [1]. For some solar-grade silicon materials, it has been observed that the PECVD process results in the improvement of bulk minority-carrier diffusion lengths as well, presumably due to bulk defect passivation [2].

In order to gain the full benefit from improved emitter surface passivation on cell performance, it is necessary to tailor the emitter doping profile so that the emitter is lightly doped between the gridlines, but heavily doped under them [3]. This is especially true for screen-printed gridlines, which require very heavy doping beneath them for acceptably low contact resistance. This selectively patterned emitter doping profile has historically been obtained by using expensive photolithographic or screen-printed alignment techniques and multiple high-temperature diffusion steps [3,4]. Recent attempts to simplify this process using screen-printed, acid-resist etchback, or laser-defined diffusion patterns still rely on precision alignment of gridlines, a process which may be difficult to implement in mass-production [5-7].

We have attempted to build on a self-aligned emitter etchback technique first described by Spectrolab [8]. In addition to the gridline-masked, plasma-etchback of the emitter they demonstrated, we have included plasma-hydrogenation treatments for bulk defect passivation combined with PECVD-nitride deposition for surface passivation and antireflection coating.

EXPERIMENTAL PROCEDURE

The self-aligned, selective-emitter (SASE) process is outlined in Figure 1. Cells using Solarex cast multicrystalline silicon received standard production line processing at Solarex through the printing and firing of the gridlines. Then, the cells were sent to Sandia for reactive ion etching (RIE) to increase the sheet resistance of the emitters to 100 ohms/square. They were plasma-etched in a Vacutec direct-plasma reactor which uses a standard dual, parallel-plate design and operates at 13.56 MHz. The etching was done using pure SF₆ at a power of 15W and a pressure of 100 mTorr for about one minute. In a second Vacute chamber, the cells received a silicon-nitride deposition and optional ammonia-plasma hydrogenation (H-passivation) treatment, both found to be effective for bulk and surface passivation in String Ribbon™ mc-Si [2]. As shown in Ref. 9, this type of high-frequency, direct PECVD-nitride film results in excellent emitter passivation and UV-stability, as good as that obtained by remote PECVD films that have produced low recombination velocities [9]. The plasma-nitride depositions were performed at 330C using pure ammonia and either a 2% mixture of silane in argon or a 5% mixture of silane in helium. The hydrogenation treatments used similar conditions with the silane flow set to zero. The cells then received a forming gas anneal (FGA) at 300C and were returned to the Solarex production-line for back metallization.

Rather than simply deposit the plasma-nitride layer in one step, we investigated whether additional performance gains could be obtained by incorporating an ammonia-plasma hydrogenation step into the deposition process. Gains in blue and red response using this approach have been previously reported, although damage to an unprotected emitter surface was also observed [2].

Therefore, we investigated a 3-step deposition technique that consisted of deposition of a thin nitride protective layer,
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followed by the hydrogenation treatment, and then deposition of the remaining thickness of silicon-nitride required for antireflection purposes. We conducted our investigation of deposition parameters using a response surface methodology approach described in Ref. 10. We began with a main-effects analysis. Then, a quadratic interaction experiment followed, which varied only the most important factors to find conditions for peak efficiency. Finally, an SASE process using the predicted optimum parameters was performed to confirm the prediction.

Table 1. Six processing sequences were applied to 12 Solarex mc-Si cells using matched material from the same ingot. Illuminated cell IV data are shown normalized to a constant transmittance to account for the different optical properties of the ARCs. Spectral absorbance in nitride layers was calculated from spectroscopic ellipsometry measurements and added to spectral reflectance [11]. Transmittance = 1-(reflectance + absorbance).

<table>
<thead>
<tr>
<th>Group</th>
<th>Technique</th>
<th>n=2.3</th>
<th>n=2.2</th>
<th>n=2.2, 15-nm prot. film</th>
<th>n=2.2, 25-nm prot. film</th>
<th>TiO₂ ARC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>RIE, 1-step SiN</td>
<td>12.6±0.0</td>
<td>28.8±0.1</td>
<td>585±1</td>
<td>75.0±0.4</td>
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</tr>
<tr>
<td>2</td>
<td>RIE, 1-step SiN</td>
<td>12.8±0.1</td>
<td>29.0±0.1</td>
<td>585±1</td>
<td>75.3±0.1</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>RIE, 3-step SiN</td>
<td>13.0±0.0</td>
<td>29.5±0.0</td>
<td>589±2</td>
<td>75.2±0.1</td>
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</tr>
<tr>
<td>4</td>
<td>RIE, 3-step SiN</td>
<td>13.1±0.0</td>
<td>29.5±0.1</td>
<td>589±1</td>
<td>75.3±0.3</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>RIE, TiO₂ ARC</td>
<td>12.9±0.1</td>
<td>29.2±0.0</td>
<td>586±1</td>
<td>75.4±0.3</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Control Cells: No emitter etchback, TiO₂ ARC</td>
<td>12.9±0.1</td>
<td>29.4±0.0</td>
<td>586±1</td>
<td>74.8±0.2</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. Process sequence for self-aligned, selective-emitter etchback. The emitter etchback can be performed after the hydrogenation treatment to remove surface damage. However, in this work, the plasma-etching was done first.

RESULTS

The first experiment was a main-effects analysis that compared 1-step and 3-step depositions using six groups of full-size 130-cm² Solarex cells processed as described in Table 1. Relative to the control cells in Group 6, the cells from Group 1 actually suffered an efficiency loss from the deposition of a 1-step nitride ARC. The SiN deposition process had drifted slightly and the nitride refractive index was slightly higher than the target value of 2.2, chosen to minimize absorption plus reflectance after encapsulation under glass [11]. As the corresponding internal quantum efficiency (IQE) curve in Figure 2 shows, this results in lower blue response.

![Figure 2. IQE curves of Solarex cells from Groups 1-6 described in Table 1, corrected for absorption in nitride films using Ref. 11.](image-url)

The Group 2 cells perform almost identically to the controls with a slightly lower Jₜₑₙₖ compensated for by a slightly higher fill factor. The extremely low IQE of all the RIE-etched cells below 350 nm, possibly due to slight surface damage from etching, may account for the lower current, while a reduction in series resistance due to plasma processing noted earlier, may account for the higher FF [12]. Groups 3 and 4 which used the 3-step deposition technique incorporating a hydrogenation step show the greatest gains in performance. These cells show efficiency gains of up to 0.2% absolute over the controls, and 0.5% over the 1-step cells from Group 1. The greatest increase in blue response is seen in the cells with the thinner protective layer, which show an IQE(400 nm) of 80%, the highest we have observed on mc-Si cells using SiN emitter passivation, with or without emitter etchback. This confirms the negligible effect of RIE surface damage on cell performance.
The Group 5 cells do not show the loss in FF due to the increased sheet resistance of the etched-back emitter noted in earlier work because these cells used more closely spaced gridlines to compensate for that effect [12].

The long-wavelength response of all the nitride-coated cells are consistently higher than that of the TiO₂-coated cells in Groups 5 and 6, presumably due to reduced bulk recombination from the plasma-nitride and hydrogenation treatments. Inverse-IQE analysis indicates that electron diffusion lengths in the bulk of cells from Groups 1-4 are typically around 130 μm, while those in cells from Groups 5 and 6 are 90 to 100 μm. This explains the somewhat higher Voc values for the 3-step cells.

**Quadratic Experiment**

Because the previous results showed that the in situ ammonia-plasma treatment in the 3-step nitride deposition process produced cells with the highest efficiency, we decided to investigate which parameters of the 3-step process would optimize cell performance. Using response surface methodology, we used a quadratic experimental design in a statistical multiparameter experiment to find the optimum parameter set. We studied the effect of 3 factors: the thickness of the silicon-nitride protective layer, and the duration and power of the plasma treatment. The factors investigated and their ranges are shown in Table 2.

Table 2. Parameters used for the Quadratic Experiment

<table>
<thead>
<tr>
<th>Parameter [units]</th>
<th>Minimum Value</th>
<th>Maximum Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness of nitride protective layer [nm]</td>
<td>15</td>
<td>35</td>
</tr>
<tr>
<td>Duration of ammonia-plasma treatment [min]</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>RF-power during ammonia plasma treatment [W]</td>
<td>20</td>
<td>50</td>
</tr>
</tbody>
</table>

The results of the quadratic experiment are contour plots of the measured variables, which in this case were illuminated cell performance parameters. The response surface for cell efficiency near the highest maximum is shown in Figure 3. It predicts an efficiency of 12.9% in a corner of the parameter space with the thinnest protective layer and maximum power and duration. This behavior suggests that even better results may be obtainable by extending the ranges of these parameters.

The 95% confidence limits associated with this contour plot show a statistical uncertainty of 0.2 percentage points in the upper-left corner due to material and process variability, implying that cells fabricated using these parameters could have an efficiency anywhere between 12.7 and 13.1%. Indeed, when 2 cells were processed using this recipe, the average efficiency was 12.7%, with the best cell reaching 12.8%. Table 3 shows the normalized IV data for these 3-step cells processed using the predicted optimized parameters as well as data for control cells, 1-step cells and cells with two kinds of double-layer ARC (DLARC) processes.

As seen before, the 1-step SASE cell shows no discernable difference in performance from that of the control cells. However, as predicted by the statistical model, the optimized 3-step cells have an average efficiency of 12.8%, which is half an absolute percentage point greater than that of the control cells. As before, the 3-step SASE cells show a slight improvement in Jsc as well as Voc compared to the controls.

Figure 4 shows that the blue response of the optimized SASE cell slightly exceeds that of the control cell. Also shown are the IQE curves of the two cells from the quadratic experiment with the highest and lowest measured currents. It is clear that the predicted optimum combination of NH₃-
plasma conditions does result in the highest IQE overall. These nitride-passivated cells used a different SiH₄ gas mixture than those in Fig. 2 resulting in slightly lower blue response.

![Figure 4. IQE curves of highest and lowest current cells from the Quadratic Experiment and the optimized 3-step and control cells in Table 3, corrected for absorption in nitride films using Ref. 11.](image)

Also shown in Table 3 are performance data from three cells with DLARC SiN layers using refractive indices and thicknesses optimized for encapsulation under glass. These cells, with efficiencies and currents normalized to the same transmittance as the controls, appear to have similar performance. However, with the lower reflectance expected of these DLARC cells after encapsulation, their performance is also expected to exceed those of the controls. The 3-step DLARC cell with the NH₃-treatment performed between the two layer depositions performs the same as the 2-step cells without the NH₃-treatment. This shows that the initial 40-nm, 2.4 index film is too thick for the hydrogenation to be effective. However, the initial high-index layer itself could be put down in a 3-step process to gain the same benefits as the 3-step single-layer ARC (SLARC).

**CONCLUSIONS**

This investigation has shown that the use of the SASE process in production-line fabrication of screen-printed solar cells results in improvement of half an absolute efficiency point over standard ARC controls. This has been done using a single, industrial emitter-diffusion process and no alignments. This process results in a well-passivated emitter surface, and a less heavily doped emitter between gridlines for reduced emitter recombination. It allows for heavier doping beneath the gridlines for lower contact resistance, reduced contact recombination, and better bulk defect gettering. Future work in this area will incorporate heavier emitter doping, optimization of a DLARC process, as well as combining bulk hydrogenation from the backsides of the solar cells.

**ACKNOWLEDGEMENTS**

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**REFERENCES**


