Research Article

17.6% Conversion Efficiency Multicrystalline Silicon Solar Cells Using the Reactive Ion Etching with the Damage Removal Etching

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For lower reflectance, we applied a maskless plasma texturing technique using reactive ion etching (RIE) on acidic-textured multicrystalline silicon (mc-Si) wafer. RIE texturing had a deep and narrow textured surface and showed excellent low reflectance. Due to plasma-induced damage, unless the RIE-textured surfaces have the proper damage removal etching (DRE), they have a drop in $V_{oc}$ and FF. RIE texturing with a proper DRE had sufficient higher short circuit current ($I_{sc}$) than acidic-textured samples without a drop in open circuit voltage ($V_{oc}$). And in order to improve efficiency of mc-Si solar cell, we applied RIE texturing with optimized DRE condition to selective emitter structure. In comparison with the acidic-textured solar cells, RIE-textured solar cells have above 200 mA absolute gain in $I_{sc}$. And optimized RIE samples with a DRE by HNO$_3$/HF mixture showed 17.6% conversion efficiency, which were made using an industrial screen printing process with selective emitter structure.

1. Introduction

In order to improve the solar cell performance, incoming light in the cell has to be coupled into the cell and transformed into electrical energy more effectively. Losses due to reflection and transmission of the incident light have to be reduced to increase the solar cell efficiency. A texture causes a multiple reflection on its surface. Therefore, the amount of collected light into the substrate, depending on the amount reflections, increases. This increase of collection, together with the larger average path length of the light in the substrate, causes an increased possibility of absorption [1].

Numerous techniques for texturing mc-Si have been examined in the past. Many approaches have been based on isotropic wet acidic etching. This method does not provide the extremely low reflection but does have the advantages of being relatively easy to implement and low cost. Some have focused on the use of RIE, either in conjunction with a mask to achieve large, regular features or without a mask to produce much smaller and more random texture [2]. RIE is a kind of plasma etching, not only the chemical etching of the plasma species, but also the kinetic energy of its ions. From the time plasma etching was applied in the semiconductor industry for patterning Si substrates, it is known that plasma etching, under certain conditions, causes a surface texture of a very high roughness [3]. Reflectivity can be minimized to below 1% [4]. Decrease in reflectivity does not automatically lead to an improvement of cell efficiency. It is known that a less rough form of this texture can be used for more effective light coupling into Si substrates [5, 6]. The reflectivity can be well controlled by RIE. This way of texturing is ideal for very fragile substrates. According to previous studies, RIE textured surface has shown extremely low reflectance [7]. However, surface damage may be caused by RIE-texturing [8] and result in a high surface recombination velocity due to the enlarged surface. RIE-textured cells have reduced quantum efficiency in the short wavelength, unless the RIE-textured surface receives the proper DRE [7]. Because problem of RIE may be that the energetic ions can introduce damage in the Si material [9], so Carriers have a large chance of...
Acid texturing
Reactive ion etching
Damage removal etching
SiO$_2$ mask deposition
SiO$_2$ mask patterning
Heavy diffusion
PSG removal
Shallow diffusion
PSG removal
PECVD SiNx deposition
Screen printing
Co-firing
Laser isolation
Cell test and analysis
Figure 1: Fabrication process for screen-printed selective emitter mc-Si solar cells with RIE texturing.

recombining at the needles of the surface and will not reach the p-n junction. In order to remove this problem, we studied DRE using HNO$_3$/HF mixture with various etching time. The aim of this work was to find DRE conditions that create a texture with a low reflectance and without a drop of $V_{oc}$ and $	ext{FF}$, which obtains a maximum improvement for $I_{sc}$ and conversion efficiency. And for high efficient mc-Si solar cell, we applied selective emitter technique on screen printing process with RIE texturing.

2. Experiment

The fabrication process is outlined in Figure 1. In this work, solar grade multi-crystalline silicon wafer of size 156 × 156 mm$^2$, boron doped p-type, was used. And resistivity 1.9 ohm-cm and thickness 200 um were taken. The isotropic texturing of mc-Si wafer was carried out by using acidic solutions. Then acid-textured Si wafers were processed in an RIE reactor. After RIE texturing, we investigated various DRE times with acidic solution (dilute HNO$_3$ and HF mixture) to determine which produces the highest cell performance with screen-printed solar cell process. A sequence with diluted KOH and HCl/HNO$_3$ treatments has been found not to affect the visual appearance of the texture structure. The textured surface was analyzed using a scanning electron microscope (SEM). SiO$_2$ layer was deposited as diffusion barrier mask. To form the selective emitter structure, mask was patterned by etch paste for heavily diffusion. These wafers was doped in conventional tube furnace using POCl$_3$ liquid source. The phosphorous silicate glass (PSG) and remaining SiO$_2$ was removed with a 10% HF solution simultaneously. A shallow diffused region is created by POCl$_3$ diffusion. After second diffusion, sheet resistance below the contact fingers were 20 Ω/□ and between fingers were 80 Ω/□, respectively. And PSG was removed with a 10% HF solution. The SiNx layer was deposited on the emitter, using direct PECVD. Refractive index and thickness of PECVD SiNx layer were 2.06 and 85 nm, respectively. Next, the Ag and Al pastes were screen-printed onto the front and back of each sample and cofired in a lamp-heated belt furnace. The cells were isolated using a laser, and the cells were tested using the solar simulator.

3. Results and Discussion

To improve cell efficiency, we applied RIE on mc-Si wafer and fabricated selective emitter mc-Si solar cells. First, we compare acidic- and RIE-textured surface morphologies and reflectance. Figure 2 shows SEM images of mc-Si wafer with acidic- and RIE-textured surfaces. Figures 2(a) and 2(c) are only acid-textured surface, which has smooth and bowl-like features. Figures 2(b) and 2(d) are RIE-textured surface on acid-textured wafer. This has many nanosized features in dent. And it has many deeper features than only acid-textured surface which provide very dark looks. As can be seen in Figure 3, RIE-textured surface have lower reflectance than acidic textured surface in all wavelength. Especially, reflectance of RIE textured surface is less than 10% in short wavelength. This is caused by deep and dense structures, as can be seen in Figure 2.

Table 1 shows the electrical performance parameters of mc-Si solar cells fabricated with acidic- and RIE- textured surface. These cells had 50 Ω/□ homogeneous emitter. As can be seen in Table 1, for the RIE-textured cell, despite the improvement in $I_{sc}$, cell efficiency decrease comes from a
Figure 2: SEM images of textured surfaces: (a) acid textured surface 5000x, (b) RIE-textured surface 5000x, (c) acid textured surface 30000x, and (d) RIE-textured surface 30000x.

Figure 3: After antireflective coating, reflectance of acidic- and RIE-textured surfaces.

Table 1: The average electrical performance of homogeneous emitter mc-Si solar cell with acidic and RIE texturing.

<table>
<thead>
<tr>
<th></th>
<th>$V_{oc}$ (V)</th>
<th>$I_{sc}$ (A)</th>
<th>FF (%)</th>
<th>Eff. (%)</th>
</tr>
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<tr>
<td>Acid texturing</td>
<td>0.626</td>
<td>8.241</td>
<td>77.97</td>
<td>16.54</td>
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<tr>
<td>RIE texturing</td>
<td>0.619</td>
<td>8.284</td>
<td>76.88</td>
<td>16.20</td>
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<tr>
<td>Difference</td>
<td>$-0.007$</td>
<td>$+0.043$</td>
<td>$-1.09$</td>
<td>$-0.34$</td>
</tr>
</tbody>
</table>

Drop in $V_{oc}$ and FF. The most main cause for this result is surface plasma damage by RIE texturing [8]. Because problem of RIE may be that the energetic ions can introduce damage in the Si material [9], so Carriers have a large chance of recombining at the needles of the surface and will not reach the p-n junction.

In order to remove plasma-induced damage, we studied DRE using HNO$_3$/HF mixture with various etching times. As can be seen in Figure 4, as DRE time increases, number of nanosized features decreases and textured surface was smoother. This result means that damaged surface was gradually removed by DRE. Figure 5 shows reflectance of acidic- and RIE-textured surfaces with various DRE times after antireflective coating. As DRE time increases, the reflectance...
Figure 4: SEM images of RIE textured surface with various DRE times (30000x): (a) No DRE, (b) DRE 20 sec, (c) DRE 40 sec, and (d) DRE 60 sec.

Figure 5: After antireflective coating, reflectance of acidic- and RIE-textured surfaces with various DRE time.

of RIE-textured surface approaches the acidic-textured surface, because the nano sized features formed during RIE process are becoming smooth by DRE. RIE-textured samples with DRE have lower reflectance than acidic-textured samples in the short wavelength region also that you can check again. So we can have a sufficiently higher $I_{sc}$ than wet acidic-textured samples.

Figure 6 shows electrical characteristics of RIE-textured mc-Si solar cells with various DRE times. Applying DRE, all electrical factors ($V_{oc}$, $I_{sc}$, FF, and efficiency) of mc-Si solar cell had better results than without DRE. It seems that this was caused by removing plasma-induced damage. As can be seen in Figure 6(a), as the DRE time increases, $V_{oc}$ was increased due to plasma damage etching. But, as the DRE time increases, $I_{sc}$ was decreased as shown Figure 6(b). This is consistent with results of Figures 4 and 5. As DRE time increases, because the reflectance of textured surface gradually was higher, $I_{sc}$ tends to decrease slightly. And we were confirmed the highest efficiency of mc-Si solar cell in DRE condition at 20 and 30 sec and achieved best cell efficiency applying homogeneous emitter structure.

To improve efficiency of mc-Si solar cell, we applied selective emitter structure with RIE texturing and optimized DRE condition. For selective emitter, SiO$_2$ layer was deposited as diffusion barrier mask and patterned by etch paste for heavily diffusion. These wafers were doped in conventional tube furnace using POCl$_3$ liquid source. The PSG and remaining SiO$_2$ were removed with a 10% HF solution simultaneously. A shallow diffused region is created by POCl$_3$ diffusion. After second diffusion, sheet resistance below the contact fingers was 20 $\Omega$/$\square$ and between fingers was 80 $\Omega$/$\square$, respectively.

Table 2 shows the result of electrical parameters of selective emitter mc-Si solar cells with acidic and RIE texturing. RIE-textured samples were applied by 20 sec DRE condition. The value of cell efficiency is average results of 5 wafers in an experiment with neighboring wafers in ingot. We achieved above 200 mA absolute $I_{sc}$ gain in 6 inch mc-Si solar
Figure 6: Electrical characteristics of RIE-textured mc-Si solar cells with various DRE times. (a) Open circuit voltage ($V_{oc}$). (b) Short circuit current ($I_{sc}$). (c) Fill factor (FF). (d) Conversion efficiency.

Figure 7: External quantum efficiency (EQE) of selective emitter mc-Si solar cells with acidic- and RIE-textured surface.

Table 2: The average electrical performance of selective emitter mc-Si solar cell with acidic and RIE texturing.

<table>
<thead>
<tr>
<th></th>
<th>$V_{oc}$ (V)</th>
<th>$I_{sc}$ (A)</th>
<th>FF (%)</th>
<th>Eff. (%)</th>
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<tr>
<td>Acid texturing</td>
<td>0.633</td>
<td>8.517</td>
<td>78.1</td>
<td>17.3</td>
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<tr>
<td>RIE texturing (DRE 20 sec)</td>
<td>0.632</td>
<td>8.685</td>
<td>77.9</td>
<td>17.6</td>
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with acidic- and RIE-textured surface, as Figure 7 shows. It is clear that the selective emitter solar cell with the RIE texturing has the improved quantum efficiency compared to acidic texturing for wavelength below 600 nm. This results in low reflectance without plasma-induced damage.

4. Conclusion

RIE texturing had a deep and narrow textured surface and showed excellent low reflectance. Due to plasma-induced damage, unless the RIE-textured surfaces have the proper DRE, they have a drop in $V_{oc}$ and FF. The 20 and 30 sec DRE times with acidic solution (HNO$_3$ and HF mixture) have the best conversion efficiency by improving the $I_{sc}$ without a drop in $V_{oc}$ and FF. In order to improve efficiency of mc-Si solar cell, we applied 20 sec DRE condition to selective emitter structure. In comparison with the acidic-textured solar cells, mc-Si solar cells with RIE texturing have above 200 mA absolute gain in $I_{sc}$. Optimized mc-Si solar cell with RIE-textured surface showed 17.6% conversion efficiency, which was made using an industrial screen printing process with selective emitter structure. And EQE measurements show the RIE texturing has the improved quantum efficiency compared to acidic texturing for wavelength below 600 nm. This result in low reflectance without plasma-induced damage.

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References


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