Temperature Effect of Nano-Structure Rebuilding on Removal of DWS mc-Si Marks by Ag/Cu MACE Process and Solar Cell

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Abstract: The absence of an effective texturing technique for diamond-wire sawn multi-crystalline silicon (DWS mc-Si) solar cells has hindered commercial upgrading from traditional multi-wire slurry sawn silicon (MWSS mc-Si) solar cells. In this work, we present a novel method for the removal of diamond-wire-sawn marks in a multi-crystalline silicon wafer based on metal assisted chemical etching process with Cu/Ag dual elements and nano-structure rebuilding (NSR) treatment to make a uniform inverted pyramid textured structure. The temperature effect of NSR solution was systematically analyzed. It was found that the size of the inverted pyramid structure and the reflectance became larger with the increase of the NSR treatment temperature. Furthermore, the prepared unique inverted pyramid structure not only benefited light trapping, but also effectively removed the saw-marks of the wafer at the same time. The highest efficiency of 19.77% was obtained in solar cells with an inverted pyramid structure (edge length of 600 nm) fabricated by NSR treatment at 50 °C for 360 s, while its average reflectance was 16.50% at a 400–900 nm wavelength range.

Keywords: solar cells; metal assisted chemical etching; inverted pyramid structure; removal of saw marks

1. Introduction

In the last few decades, multi-wire-slurry-sawing (MWSS) has been the mainstream technique to slice large ingots of single/multi-crystalline silicon (mc-Si) into thin wafers in the photovoltaic (PV) industry [1,2]. However, MWSS has several drawbacks such as possible environmental contamination and higher ingot and material consumption (e.g., silicon itself and steel-wire) [3,4]. Comparatively speaking, the diamond-wire-sawing (DWS) technique benefits from higher productivity, lower wear of the wire, and easier recycling for the cooling process [5]. Thus, it has been considered as an upgrade to MWSS and has been widely put into use in the solar industry.

Due to its poor surface conditions (i.e., not enough reaction starting points), the DWS mc-Si wafer could not be textured by traditional method with HF/HNO 3 [6]. Randomly distributed amorphous silicon layers and parallel saw marks were generated by the diamond wire cutting process. It was reported that the amorphous layer would stop the texturing process, as confirmed by Raman spectroscopy, to a certain extent [7,8], and the heavy saw marks could not be easily textured by the current acid texturing process causing the solar cells to suffer a serious decrease in current and voltage.
The metal-assisted chemical etching (MACE) technique is a cost-effective way to prepare a nano-scaled texturing surface whose morphology provides a very good light trapping condition for the wafer surface, which ultimately resulted in a low reflectance for solar cells [9-11]. In addition, many researchers have demonstrated that this “black silicon” structure could be prepared homogeneously, regardless of the wafer surface condition, which means that even an amorphous silicon layer could be etched off [12]. Through the MACE process, noble metals with higher electronegativity than Si such as Au, Ag, and Cu were used as a catalyst to speed up the etching process on the Si surface [13]. Cu was found to be the cheapest metal that could be used for the MACE method. However, the etching rate with copper is very low at room temperature, which is not fit for industrial use. Recently, it was demonstrated that the etching rate with Cu assisted at 60 ºC was 11 times larger than that of the reaction at room temperature [14], by which it could be applied in mass production.

In this paper, a Cu and Ag dual element combined catalyst was applied at room temperature to prepare anti-reflectance structures on a solar-grade mc-Si wafer. This was followed by a post acid treatment by nanostructure rebuilding (NSR) solution at different temperatures to obtain nano-scaled regular inverted pyramid structures. We show that this method can effectively remove saw marks on the wafer surface and increase light trapping performance to achieve an outstanding conversion efficiency over 19.77% on a DWS mc-Si substrate under AM 1.5 G illumination.

2. Materials and Methods

P-Type DWS mc-Si and MWSS mc-Si (180 ± 10 µm thick, 1–3 Ω·cm) wafers with a size of 156.75 × 156.75 mm² were chosen in this work. Acid texturing was applied in the baseline group to remove the mechanical damage of the wafer surface and to obtain an oval pit texturing layer. For the MACE group, the wafer was first etched in a mixed solution of 5.8 M HF (hydrofluoric acid) and 0.6 M H₂O₂ containing 2.4 mM Cu (NO₃)₂ and 0.06 mM AgNO₃ for 180 s to form nanopore structures. Then, the wafer was immersed into an ammonia and H₂O₂ mixed solution over 180 s to remove the metal particles from the previous etching process step. After rinsing in 5 wt.% HF and deionized (DI) water system, wafer surface was treated in a NSR solution (2.52 M H₂O₂ and 0.42 M NaF) for 360 s with different temperatures (30 ºC, 40 ºC, 50 ºC, 60 ºC). Finally, this textured wafer was fabricated into a screen-printed solar cell with a series of processes that included phosphorus diffusion, phosphosilicate glass (PSG)-removal, edge isolation, anti-reflection (AR) coating, printing, and firing.

The surface morphology was characterized by scanning electron microscopy (Hitachi S-4800). For the wafer surface reflectance measurement, it was carried out by a UV–Vis–NIR spectrophotometer (Shimadzu, UV-3600, with an integrating sphere) between the wavelength range of 300 to 1100 nm.

3. Results

Comparison of Acid Texturing for the DWS Wafer and MWSS Wafer

The surface morphology of the DWS and MWSS wafer before and after acid texture were shown in Figure 1. For the baseline group (Figure 1a), the heavy surface damage of the MWSS wafer was evident as deep fissures and cracks acted as a seeding layer to accelerate the reaction for the acid texturing. The textured pattern with equally distributed oval pit structures by classical acid texturing process on the MWSS wafer surface is shown in Figure 1b. However, for the DWS wafer (Figure 1c), there were parallel saw marks, disperse pits, and amorphous layer (~20 nm) due to ductile cutting process [15]. After acid texturing of the DWS wafer, as shown in Figure 1d, the saw marks still existed, but a few oval pit structures appeared. Saw marks and the amorphous layer were the main reasons for the invalidation of the texturing process, as it was reported that the amorphous layer would hinder the etching process in an acidic system [16,17]. Figure 2 compared the reflectance curves of MWSS wafers and DWS wafers after the texturing process. The reflectance of textured DWS wafer was still higher than the as-cut MWSS wafer due to its bad surface conditions such as saw marks and smooth regions caused by amorphous layers [18]. The average reflectance (400–900 nm) from both
the wafers decreased after the acid texturization process. For the MWSS wafer, it reduced by 5.32%. In contrast, the reflectance of DWS wafer was reduced by only 3.55%. The average value of 29.42% at the 400–900 nm wavelength range was 6.27% higher than that of the MWSS wafer after the acid texturing process (23.15%).

![Scanning electron microscope (SEM) images of the structure before and after acid texture: (a) as-cut MWSS wafer; (b) MWSS wafer after acid texture; (c) as-cut DWS wafer; (d) DWS wafer after acid texture.](image)

**Figure 1.** Scanning electron microscope (SEM) images of the structure before and after acid texture: (a) as-cut MWSS wafer; (b) MWSS wafer after acid texture; (c) as-cut DWS wafer; (d) DWS wafer after acid texture.

![Reflectance curves of MWSS wafer and DWS wafer before and after acid texture.](image)

**Figure 2.** Reflectance curves of MWSS wafer and DWS wafer before and after acid texture.

For the first step of this Cu/Ag assisted MACE method, a bare DWS wafer was etched in a mixture solution containing Cu$^{2+}$ and Ag$^+$ ions. As shown in Figure 3a, at the beginning of the reaction, H$_2$O$_2$ performed as an oxidation agent to oxidize Si atoms on the wafer surface to SiO$_2$ in the position where the metal particles and the Si surface were in contact with each other. The formed SiO$_2$ was then removed by HF to form nanopore structures. Moreover, some groove-like structures appeared in the inset figures, which may be due to the catalytic properties of Ag preferential etching along the $<100>$ crystallographic orientation of Si. However, the Cu assisted etching process would not follow the settled crystallographic orientation, since it is an isotropic etching process. It is worth mentioning that the Cu assisted etching process needs a rough surface to start the reaction [19,20]. This is the root cause of very low reaction speeds at room temperature. As a result, a very small dosage of AgNO$_3$ was induced into this etching solution as a catalyst to form nanostructures at the very beginning of the reaction. Consequently, the etching rate of Cu was accelerated. These composite structures with nanopores and grooves showed good light trapping ability with an average reflectance of lower than 6.23% at the 400–900 nm wavelength range.
with an edge length ranging from 100 nm to 150 nm. In another group, the square pores were treated further with the NSR solution at 40 °C. As seen in Figure 3c, formation of the <111> pyramidal orientation started to appear in the bottom of some shallow pores. With further increase of the NSR treatment temperature, the decomposing rate of H2O2 accelerated so much so that it caused a serious reaction condition. As shown in Figure 3e, after the NSR process for 360 s at 50 °C, the square pores nearly disappeared and became the regular invert pyramids with an edge length of 600 nm. When the NSR treatment temperature reached 60 °C, those small inverted pyramid structures interconnected to become bigger ones, the surface became flatter, and the inverted pyramid edge length turned to be over 900 nm.

It is reported that the anti-reflection properties would be better if the inverted pyramids became larger [21]. However, the results showed the opposite. Figure 4 shows the reflectance values and outline pictures of the NSR treated samples for different times. The as-etched sample with nanopore structures showed the lowest reflectance with an average value of 6.23% between the 400–900 nm wavelength range. The outline of this sample was totally black. As we can see, the reflectance of these samples was higher with the increase of the NSR treatment temperature. The reflectance even reached 20.46% when the NSR treatment temperature was 60 °C. This value was close to the reflectance of the acid-textured MWSS samples but was still lower than that of the DWS wafer (29.42%). However, the samples with 50 °C NSR treatment showed an appropriate reflectance of 16.50% at the 400–900 nm wavelength range. Additionally, the inverted pyramids with an edge length of 600 nm could also bear possible damage during the following processing steps including diffusion, PSG etching, and PECVD [22].

It was reported that the saw marks caused by the DWS process would lead to a serious electrical loss that could greatly reduce the open circuit voltage (Voc) of solar cells [23]. After the NSR solution treatment for 180 s at 50 °C, the saw marks became shallow and nearly disappeared. As shown in Figure 5, they were full of inverted pyramid structures distributed on the Si surface and their edge length was about 600 nm. This demonstrated that the saw marks were almost eliminated during the process.
The increased NSR treatment temperature and so did the reflectance. Furthermore, we have proved and morphology of the textured silicon surface. Size of the inverted pyramid became larger with the increased NSR treatment temperature due to the disappearance of surface defects (saw marks and nanopores). After the surface defects were almost eliminated, the value of Isc showed an inverse trend resulting from the increased reflectance.

When the NSR treatment temperature increased to 50 °C, with the saw marks and nanopores disappearing, the NSR-50 °C cells achieved an excellent efficiency over 19.77%, which was 0.54% higher than the baseline group. The NSR-60 °C cell showed a decreased in Isc compared with NSR-50 °C due to its higher surface reflectance (20.46% compared to 16.50% in the former). Even so, it still had a relatively high efficiency of 19.59% compared with conventional cells. We could deduce that the Isc increased with NSR treatment for 180 s at 50 °C due to its higher surface reflectance (20.46% compared to 16.50% in the former). Even so, it still had a lower reflectance.

Table 1 illustrates the cell final performance including open circuit voltage (Voc), short circuit current (Isc), fill factor (FF), and efficiency (Eff) of the BS, NSR-30 °C, NSR-40 °C, NSR-50 °C, and NSR-60 °C solar cells (the corresponding structures were shown in Figure 3). Obviously, due to the serious Auger recombination rate of photogenerated carriers caused by surface defects including saw marks and nanopores, the solar cells of BS, NSR-30 °C, and NSR-40 °C showed relatively lower values of Isc, Voc, and Eff compared to the other two cells, even though they had a lower reflectance.

Table 1. Main characteristics of six types of solar cells.

| Cell Type     | Isc (A) | Voc (mV) | FF (%) | Eff (%) |
|---------------|---------|----------|--------|---------|
| Standard cells| 8.908   | 660      | 80.37  | 19.23   |
| BS            | 8.610   | 642      | 78.50  | 17.66   |
| NSR-30 °C     | 8.781   | 649      | 79.12  | 18.35   |
| NSR-40 °C     | 8.931   | 659      | 79.15  | 18.96   |
| NSR-50 °C     | 9.132   | 662      | 80.39  | 19.77   |
| NSR-60 °C     | 9.061   | 661      | 80.37  | 19.59   |

Figure 4. Reflectance values and outline pictures of the NSR treated samples for different times.

Figure 5. SEM image of the etched sample (a) without or (b) with NSR treatment at 50 °C for 180 s.

4. Discussion

Overall, our studies have established the relationship between the temperature of the NSR solution and morphology of the textured silicon surface. Size of the inverted pyramid became larger with the increased NSR treatment temperature and so did the reflectance. Furthermore, we have proved...
that the unique inverted pyramid structure not only benefited light trapping for the cell, but also effectively removed the saw-marks of the DWS wafer simultaneously, which will be an industrial friendly process for saw-mark removal and texturing. In our future research, we might transfer this process to a mono-crystalline wafer for the mono PERC process to gain more current and reduce the surface pyramid cusp recombination.

5. Conclusions

A novel texturing process assisted by the Cu/Ag combined system and NSR process was developed to successfully form uniform antireflection structures and to remove almost all the saw marks. An inverted pyramid structure could be prepared by following a NSR solution treatment and the treatment temperature was found to be the main factor affecting the size of the inverted pyramid structure and the reflectance. Both of them were larger with increasing NSR treatment temperature. The saw marks were removed in wafers produced by the Cu/Ag MACE and NSR process at 50 °C for 360 s, showing inverted pyramid structures with an edge length of 600 nm and an average reflectance of 16.50%. Using the optimized parameters, the highest efficiency of 19.77% was obtained, which was 0.54% higher than that of standard solar cells. We believed that the process in this work has the potential to be applied in the mass production of mc-Si solar cells fabricated using diamond wire sawn wafers.

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