Fabrication of micro-nano composite textured surface for slurry sawn mc-Si wafers cell

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Abstract. In order to enhance the PV efficiency of the cell made from slurry sawn (SS) mc-Si wafers, using a Ag-assisted electroless etching (AgNO3+HF+H2O2) combined with an auxiliary etching (HF+HNO3) the RENA textured SS mc-Si wafers (called as RENA wafers) were further textured (nano pores were formed on the original micro pits) to change into micro-nano composite textured wafers (called as MN-RENA wafers). The solar cells made from the MN-RENA wafers had a better PV efficiency than that of RENA wafers. This is mainly attributed to the higher light-trapping of the micro-nano composite texture. The nano size texture enhanced the light-trap of wafer surface and, at the same time, the micro size texture maintained the light-trap uniformity of different gains of RENA wafer. However, there still exist a potential for optimization, such as, the SiNx passivation coating should be improved to be deposited more uniformly in order to passivate the bottom of pits better and to reduce the reflectance of the obtuse tips of pits.

1. Introduction

RENA wafers have been widely used to fabricate PV cells, but they have a higher surface light reflectance, which results in a lower PV efficiency. Therefore, the black Si cell has been developed using metal-assisted electroless texturing and has been got a much attention [1]. Recently, diamond wire sawn (DWS) is expected to be the mainstream wafering technology in Si-based photovoltaic industry. The advantages of this technique over the conventional slurry sawn (SS) include higher productivity, higher precision enabling production of thinner wafers, less wire consumption, lower environmental impact, easier recovery of silicon kerf loss and less surface mechanical damages [2-5]. However, DWS Wafers differ from SS ones in saw damage, making standard or traditional HF+HNO3 etching mixture less suitable to achieve the desirable surface textures in the wafers [6-8]. The optimization of etching mixture formula and etching parameters (e.g. etching time, temperature) based on the traditional HF+HNO3 etching mixtures system are also not suitable for a successful texture of DWS wafers [6]. Therefore, the DWS wafer texturing has been implemented successfully using Ag-assisted electroless etching recently [9,10]. In the work [9], AgNO3+HF+H2O2 etching was applied to ensure forming pores on the smooth surface of a DWS wafer to form nano-porous Si layer, the auxiliary etching with HF+HNO3 solution was needed to make this porous Si layer develop a macroporous Si layer with sub-micron pits in order to avoid heavily doped defects on the nano-porous Si
layer during the afterwards phosphorus doping process [11,12]. Unfortunately, among the grains with
different crystal orientation there existed the differences in the axial direction and the depth of nano-
pores during AgNO3+HF+H2O2 etching. These differences resulted in the final different texture
structures after HF+HNO3 etching, which limits the efficiency of Si cells [13]. In this paper, SS mc-Si
wafers were textured using RENA texturing at first, then, the RENA textured wafer was further
textured (nano pores formed on the micro pits of RENA wafer using Ag-assisted electroless etching
(AgNO3+HF+H2O2) and, at last, the nano pores were enlarged into submicron pits using an auxiliary
etching (HF+HNO3). As a result, there formed a micro-nano composite textured surface. This
composite textured surface eliminate both the higher surface light reflectance of RENA textured
surface and the different textures between different grains on a flat surface etched using Ag-assisted
electroless etching combined with (HF+HNO3) an auxiliary etching, so that the cells made from the
wafers with the composite textured surface had a higher efficiency. Also, the problems resulted from
submicron pits on the composite textured surface were investigated in detail.

2. Experimental

SS mc-Si wafers were supplied by Linuo Solar Power Holdings Co., Ltd and textured using traditional
HF+HNO3 etching (called as RENA texturing) on the standard texturing line in this company.

Ag-assisted electroless etching (AgNO3+HF+H2O2) combined with an auxiliary etching
(HF+HNO3) was used for RENA wafers. Ag-assisted electroless etching (AgNO3+HF+H2O2) was
divided into two sub-steps: HF+AgNO3 etching and HF+H2O2 etching. The whole texturing process
consisted of seven steps. From Step 1 to Step 6, RENA wafers were immersed successively in the
aqueous solution specified as flowing and rinsed in deionized water (DIW) at room temperature (RT)
for 20 s after each step.

1. Several concentrations (0.1, 0.2, 0.5, 1 and 2mM/L) AgNO3: 1.15M/L HF, RT for different
times, to deposite Ag catalysts.
2. 4M/L HF: 0.7M/L H2O2, RT for different times, to form nano-pores.
3. 1.3M/L HF: 4.9M/L HNO3, RT for different times, to enlarge nano-pores into sub-micron pits
and remove Ag catalysts [9].
4. 6.95% (w/w) KOH, RT for 10 s, to remove Si stain [9].
5. 0.2mM/L H2O2: 0.2mM/L HCl, RT for 5 min, to remove metal ions.
6. 4.9M/L HF, RT for 1min, to remove SiO2 layer.
7. Hot air drying, 135 °C for 2 min.

The above MN-RENA wafers were made into solar cells on a standard solar cell manufacturing
line.

The morphologies of the wafers were observed using a laser scanning confocal microscope (LSCM,
OLS4000) and a S4800 scanning electron microscope (SEM). The reflectivity of the textured wafers
and the PV properties of solar cells were characterized respectively using a reflectometer (R9000-
2DMA) and a photovoltaic cell testing apparatus (Berger PSS10).

3. Results and discussion

Figure 1(a) shows the surface structure of as cut SS mc-Si wafer. The sizes of structures on the Si
surface range from 1 to 3μm. The structure is called mechanical damages resulted from the wafer
cutting and must be removed before texturing. After RENA texturing, the surface of RENA wafer
contains wormlike pores with width ranging from 2 to 4μm and random length, as shown in Figure
1(b).

The RENA wafer was deposited with Ag particles and etched in HF+H2O2 etching solution, as
described in experimental section. Its surface structure is shown in Figure 2. It can be seen that the
nano pores formed on the RENA wafer. The average diameter of the nanopores on the surface of
RENA wafer is about 10nm [14]. Figure 3 shows the spectra of light reflectivity of the as etched
wafers. For the sake of comparison, the spectra of light reflectivity of the RENA wafer are also shown
in both Figure 3(a) and (b).
In Figure 3(a), with the increase of AgNO$_3$ concentration from 0.1mM/L to 0.5mM/L, the average reflectivity of the silicon wafer surface decreased from 7.7% to 4.4%. When the AgNO$_3$ concentration increased from 0.5mM/L to 2mM/L, the average reflectivity of the silicon wafer increased slightly from 4.4% to 4.9%. In Figure 3(b), the AgNO$_3$ concentration of 0.1mM/L was selected and the deposition time of Ag was from 60s to 180s. Under such etched condition, the RENA wafers were deposited with Ag particles and etched in HF+H$_2$O$_2$ etching solution, as described in experimental section. With the deposition time of Ag increased from 60s to 180s, the surface reflectivity of the wafers decreased from 7.7% to 3.9%. While with the deposition time of Ag continued increase to 180s, the surface reflectivity increased from 3.9% to 4.1%.
pores formed under Ag particles increased and the reflectivity of wafer surface decreased. When the amount of deposited Ag reached a certain value, the Ag particles accumulated to form dendrites, which hindered the contact between the etching solution and the silicon substrate, and then hindered the Ag catalytic etching in next step. Therefore, when the AgNO$_3$ concentration was over 0.5mM/L under the deposition time of 60s or the Ag deposition time was over 120s under the AgNO$_3$ concentration of 0.1mM/L, the reflectivity of the wafer surface increased, as shown in Figure 3a and b respectively. Therefore, for the lower or higher concentration of AgNO$_3$ solution, the appropriate amount of Ag deposition of can be obtained by adjusting the Ag deposition time.

On the micro-nano size structured surface described above, there existed nano pores, which could be heavily doped and became defects during the afterwards phosphorus doping process[11,12]. Thus, the auxiliary etching with HF-HNO$_3$ solution was needed to make this porous Si layer develop into a macroporous Si layer with sub-micron pits, the surface with which is called a sub-micro size surface [13], so that the Step 3 and 4 of texturing process as described in experimental section were carried out. Meanwhile, Ag particles in the nano pores were dug out [9].

Figure 4 shows the micrographs of sub-micro size surface of wafer. It can be seen that, there formed sub-micron pits on the surfaces of the micro size pits. The formation process of the sub-micron pits is the combination of pores or pits step by step [13]. The aim of sub-micron pits formation on the surfaces of the micro size pits was to enhance the effect of light-trapping and reduce the color difference between different Si grains [15].

![Figure 4. Micrographs of sub-micro size surface of wafer](image)

(a) plan view   (b) section view

The spectra of light reflectivity of the wafers with the sub-micro size surface after different HF-HNO$_3$ etching times are shown in figure 5. The as textured wafer after etching Step 2 described in experimental section has a lowest reflectance, as shown by Curve A. With increasing the HF-HNO$_3$ etching time, the reflectance of the samples increases. The curve of the reflectance rises up from Curve A to Curve E. Curve F represents the reflectance of the RENA wafer. The increase of reflectance of the sample is resulted from the enlargement of diameter of pores or pits on the surface of wafer during the HF-HNO$_3$ etching and the longer the etching time, the bigger the diameter is [13].

In the preparation process of Si solar cells, the SiNx coatings on the surface of the wafer using PECVD have two main functions: (1) as an antireflection, further reduce the surface reflectance according to the principle of optical interference; (2) as the surface passivation, reducing the surface recombination rate to improve the effective minority carrier lifetime.

The passivated surface is shown in Figure 6. It can be seen from the figure that after coated, the pits on the surface of the wafer changed into smaller ones, and that there is an agglomeration phenomenon of SiNx on the peaks between pits. During the PECVD of the coating, the active groups involved in the reaction diffused into the pits. The active groups were more difficult to diffuse into the bottom of pits than other positions. On the contrary, near the pits opening the reaction gases were easy to exchange, so that the film formed easily. As a result, as the reaction was carried on the coating near the pits opening became thicker and thicker, so that the agglomeration of SiNx formed. Meanwhile,
the agglomeration hindered the active groups to enter into the pits and the passivation at the bottom of pits became worse.

![Figure 5](image-url)  
**Figure 5.** The spectra of light reflectivity of the wafers with the micro-nano size texture after different HF-HNO₃ etching times  
Notes: 1) no F-N means no HF-HNO₃ etched: the as textured wafer after etching Step 2  
2) F-N means HF-HNO₃ etched: the as textured wafer described in Note 1 were further etched in 1.3M/L HF: 4.9M/L HNO₃, RT for different times.  
3) +PE means samples were deposited with SiNx passive coating using PECVD.

![Figure 6](image-url)  
**Figure 6.** Comparison between as sub-micro size textured surface (a) and SiNx coated sub-micro size textured surface (b)

Through the experiment and optimization, the main process of RENA wafers cells and its parameters are listed as follows: 0.1mM/L AgNO₃-1.15M/L HF solution for 60s, 0.7M/L H₂O₂-4M/L HF solution for 120s, 1.3M/L HF-4.9M/L HNO₃ solution for 60s, 1% NaOH solution for 10s etching, the square resistance of the wafer about 90Ω/□ after P diffusion, thickness of SiNx passivation coating about 90nm and the rest of the process of SS mc-Si wafers cells is as the same as that used in traditional SS mc-Si wafers cell production line. The average value of PV properties of solar cells
made from RENA wafers, which acted as a reference group, and micro-nano textured wafers are listed in Table 1.

| Count | Uoc/V | Isc/A | Rs/Ω | Rsh/Ω | FF% | Ncell/% | Irev/1 |
|-------|-------|-------|------|-------|-----|---------|--------|
| Reference Group | 385 | 0.6287 | 8.847 | 0.0020 | 283.4 | 78.76 | 18.00 | 0.088 |
| Experimental group | 375 | 0.6291 | 9.031 | 0.0022 | 233.1 | 78.64 | 18.36 | 0.091 |

As can be seen from the table, $U_{oc}$ of the experimental group and the reference group was almost the same, but $I_{sc}$ of experimental group increases obviously compared with the reference group. This is mainly due to the lower reflectivity of silicon wafer surface of the experimental group. As a result, the average $N_{cell}$ of the experimental group was 18.36%, 0.36% higher than that of the reference group.

4. Summary

The RENA wafers have been textured successfully using a Ag-assisted electroless etching ($\text{AgNO}_3$+HF+ $\text{H}_2\text{O}_2$) combined with an auxiliary etching (HF+HNO$_3$). The solar cells made from the MN-RENA wafers had a better PV efficiency than that of RENA wafers. This is mainly attributed to the higher light-trapping of the micron-nano composite texture. The nano size texture enhanced the light-trap of wafer surface and, at the same time, the micro size texture maintained the light-trap uniformity of different gains of RENA wafer. However, there still exist a potential for optimization, such as, the SiNx passivation coating should be improved to be deposited more uniformly in order to passivate the bottom of pits better and to reduce the reflectance of the obtuse tips of pits.

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