INTRODUCTION

HIT (Heterojunction with Intrinsic Thin-layer) structure solar cell was invented by SANYO Electric Co., Ltd. in 1991.\(^1\) It is an improved version of SHJ solar cell, introducing a thin intrinsic a-Si:H (hydrogenated amorphous silicon) layer between the doped a-Si:H layer and the c-Si (crystalline silicon) substrate. HIT solar cells have many advantages, such as low fabricating temperature (<200\(^\circ\)C), high Voc (open circuit voltage, >740 mV), good stability, and the ability of absorbing light from double sides, resulting in a high conversion efficiency.\(^2\) Because HIT has been registered as a trademark by SANYO (bought by Panasonic in 2008), we still refer this type of solar cells such as SHJ cells in this paper.

The manufacturing of SHJ cells usually consists of four steps: surface texturing, a-Si:H film deposition, TCO (transparent conductive oxide) film coating, and screen printing. The performance of SHJ solar cells is largely governed by the passivation quality of a-Si:H. One approach for improving the passivation quality is preparing a clean wafer surface with appropriate morphology, which is suitable for the low defects a-Si:H film deposition. A good surface morphology is often obtained through texturing and CP etching. With the assistance of additives, \(<100>\) oriented silicon wafer is etched anisotropically in alkaline solution, forming a pyramid morphology.\(^3\) The main purpose of texturing is to improve the light-trapping effect. Furthermore, a-Si:H film deposited on (111) surface is of less epitaxial growth than on (100) surface, enhancing the minority carrier lifetime and resulting in higher Voc (open circuit voltage) for SHJ cells.\(^4\)

It has been confirmed by lots of experiments that a perfect (111) pyramid profile is not the optimal surface morphology
for a-Si:H passivation. Epitaxial growth is prone to take place in pyramid valleys, this causes the formation of defects in the a-Si:H film. Chemical polishing is an effective way to modify the pyramid profile. A common method of chemical polishing is etching textured wafer in an HNO₃ + HF solution, which has been applied on an industrial scale in Panasonic’s HIT solar cell factories. In recent years, ozone-based bath has been introduced as an alternative cleaning process, which is more environmentally friendly than traditional RCA cleaning. The ozone-based method of chemical polishing is carried out in an O₃ + HF solution, avoiding pollution emission of nitrogen. However, the influences of these two CP etching methods on the pyramid profile have not yet been compared in detail. In this work, it is found that these two methods produce different effects on the pyramid profile, such as roundness of pyramid peaks and valleys and peak angles. Furthermore, the combination of them makes new effects on the performance of SHJ cells.

2 | EXPERIMENTAL

N-type Cz wafers with <100> orientation were used in the experiment. The length × width × thickness and resistivity of the wafers were 156.75 × 156.75 × 0.15 mm and 1-2 Ω cm, respectively. The area of the wafer was 24 432 mm². The texturing and cleaning procedures included the following steps: SC1 → SDE → Tex → SC1 → CP → SC2 → HF → Dry. The solution composition, temperature, and process time of each step are listed in Table 1. Between every two steps, wafers were rinsed in flowing deionized water for 3 minutes. The texturing additives TK81 and TT72C13 are produced by Hayashi Pure Chemical Ind., Ltd. There were two kinds of CP solutions, CP1 consisted of 68%HNO₃ and 0.2%HF, and CP2 consisted of 80 ppm O₃ and 0.8%HF. The two CP methods with various etching time were compared in this work. Other researches showed that CP etching would reduce the surface-alkaline contamination. In order to eliminate the difference of surface cleanliness, wafers treated with different CP methods were cleaned again as following steps: SC1 → SC2 → HF → Dry. Hence, the differences between wafers would mainly come from the different pyramid profiles.

Following surface treatment, intrinsic a-Si:H doped n and p layers were deposited by PECVD (plasma-enhanced chemical vapor deposition), with the thickness of about 8, 8, and 10 nm, respectively. After that, TCO film coating and screen printing were performed. The TCO film coating was carried out with a PVD (physical vapor deposition) equipment by magnetron sputtering. The PVD target material was ITO (90wt% In₂O₃ + 10wt% SnO₂). The final structure of SHJ cells was Ag-gridITO(n)a-Si:H(i)a-Si:H(n)c-Si:H(i) a-Si:H(p)a-Si:HIIITO|Ag-grid. Minority carrier lifetime and implied Voc were measured on Sinton WCT-120. All lifetimes quoted are at a minority carrier injection level of 10¹⁵ cm⁻³. I-V characteristics of cells were measured at 25°C under AM 1.5 conditions.

3 | RESULTS AND DISCUSSION

3.1 | Effects of CP etching on pyramid profiles

Figure 1(A) shows the SEM image of a textured wafer without CP etching. The image is side view of the pyramids, so the roundness of peaks and valleys can be seen clearly. As shown in Figure 1(A), pyramid peaks and valleys are very sharp. Figure 2 shows the different effects on the profile of pyramids adopting different CP etching methods. While etching textured wafers in CP1 solution, the pyramid valleys become rounder as time increases, whereas the pyramid peaks remain sharp. While etching in CP2 solution, the pyramid peaks become rounder as time increases, whereas the pyramid valleys have no significant change. The reflectivity of the wafers under all the CP etching conditions are shown in Figure 3. The two CP etching methods have similar effects on the reflectivity. No matter the rounding of peaks or valleys enlarges the reflectivity.

The etching process for Si wafer in CP1 solution could be described as the following reactions:

\[
\text{Si} + 4\text{HNO}_3 \rightarrow \text{SiO}_2 + 4\text{NO}_2 + 2\text{H}_2\text{O} \tag{1}
\]

\[
\text{SiO}_2 + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O} \tag{2}
\]
The etching rate of Si wafer in CP1 solution is shown in Figure 4(A). In the first 2 minutes, 4.7 mg Si is etched from one side of the wafer, which may consume 20 mg HF, equal to the amount of HF in a 0.4 mm thickness region of solution over the wafer. Because CP1 solution consists of a very high concentration of HNO₃ and a relatively low concentration of HF, the HF in the region near the wafer surface is depleted soon. The solution is stationary while etching and there is no fluid convection, therefore, the HF is transferred to the wafer by diffusion. As the etching reaction proceeds, the diffusion distance of mass transfer is increasing gradually and the etching rate is decreasing. Finally, the etching rate is controlled by diffusion, including the diffusion of HF toward the wafer and the diffusion of reaction products away from the wafer. When the mass transfer and reaction are in equilibrium, the etching rate becomes stable. This is in consistent with the results of Steinert's research.¹⁶

It is worth noting that there is an obvious rising in etching rate at 10 minutes, this might result from the rising of temperature. The etching process is an exothermic reaction, and the temperature in a small zone near the wafer surface might rise gradually because the heat transfer is slow in a stationary solution with no fluid convection. However, the temperature near the wafer surface has not been measured in this work, and further study needs to be conducted. The average angle of pyramid peaks is measured from SEM images. The peak

Figure 1: A, SEM image of textured wafer without CP etching. B, SEM image of wafer with combined CP etching. The wafer was etched in CP1 solution for 4 min, subsequently etched in CP2 solution for 4 min.

Figure 2: SEM images of CP etched wafers using the two CP methods with various etching time.

Figure 3: Reflectivity (average value between 400 and 1100 nm) as a function of CP etching time for CP1 and CP2.
angle is 78.8° before etching, and have no remarkable change with etching time, as shown in Figure 4(B).

The etching process for Si wafer in CP2 solution could be described as the following reactions:

\[
\text{Si} + 2\text{O}_3 \rightarrow \text{SiO}_2 + 2\text{O}_2 \quad (3)
\]

\[
\text{SiO}_2 + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O} \quad (4)
\]

The concentration of O$_3$ in CP2 solution is very low, thus the O$_3$ near the pyramid surface is depleted soon. In the first 2 minutes, 3.7 mg Si is etched from one side of the wafer, which may consume 12.6 mg O$_3$, equal to the amount of O$_3$ in a 6.5 mm thickness region of solution over the wafer. The concentration of HF in CP2 solution is not high either. In the first 2 minutes, 15.7 mg HF is consumed, equal to the amount of HF in a 0.08 mm thickness region of solution over the wafer. The distance of 0.08 mm is much greater than the pyramid height of 1-4 μm. Therefore, the etching rate is dominated by the diffusion of O$_3$ and HF toward the pyramids. As the O$_3$ and HF are being consumed, the etching rate is decreasing, and then remaining stable relatively. The angle of pyramid peaks increases from 78.8° to 83.6° while etching time increasing to 10 minutes, as shown in Figure 4(B).

Based on the results above, we deduced the etching mechanism for CP1 and CP2, as shown in Figure 5. For the case of CP1, the concentration of HF at pyramid valleys is lower, and the reaction products are difficult to diffuse away from the narrow valleys, resulting in a gradient etching rate in the valley area, so the pyramid valleys are rounded gradually.
Extrapolating from the sharp peaks (Figure 2) and unchanged peak angles (Figure 4(B)), the upper area of pyramids is etched homogeneously. Neglecting the inhomogeneous etching in valleys, the etched 4.7 mg Si is equal to a thickness of 47.7 nm within the pyramid surface.

For the case of CP2, both HF and O₃ near the pyramid are depleted quickly, and the etching rate of valleys is very slow, only the upper area of pyramids is able to contact with HF and O₃ sufficiently. The etching rate of the upper area is inhomogeneous, decreasing from the peak to the valley. On the other hand, the reaction products from the valleys are too little to accumulate, thus there is no significant difference in etching rate in the valley area. As a result, the pyramid peaks are rounded, and the angle of pyramid peaks increases, whereas the valleys, have no effect of rounding. Besides this deduction, whether the peaks and the valleys have different reaction activities in different CP solutions needs further investigation.

Therefore, CP1 and CP2 solutions have different rounding selectivity, CP1 rounds pyramid valleys, whereas CP2 rounds pyramid peaks. By adjusting the etching time in CP1 and CP2 solutions, it is possible to modify the pyramid profile with different rounding levels for valleys and peaks, respectively.

### 3.2 Effects of CP etching on the passivation quality

Figure 4(C) and (D) show the minority carrier lifetime and implied Voc of passivated wafers with different CP treatments. Without any CP treatment, lifetime and implied Voc are very low, being 172 μs and 0.662 V, respectively. The sharp peaks and valleys are not suitable for a-Si:H deposition, which may cause epitaxial growth and stress in the a-Si:H layer.⁵,¹⁰ When a-Si:H layer is deposited, discontinuous silicon surfaces can act as growing sites, causing the partial epitaxial silicon to grow.¹⁷ Defects at the areas of sharp peaks and valleys accelerate the carrier recombination, thus decrease the lifetime and implied Voc.

For CP1 etching, both lifetime and implied Voc increase at first, and then decrease slowly as etching time increases. The possible reason for the decreasing of passivation quality could be the sharpening of peaks. Unfortunately, the SEM resolution is not as high to recognize the slight variations of peaks. The highest lifetime and implied Voc are 3352 μs and 0.740 V, respectively, with the etching time of 4 minutes. For CP2 etching, while etching time increasing, lifetime increases gradually and implied Voc rises rapidly in the first 2 minutes, then increasing slowly. From this phenomenon, it seems like the rounding of pyramid valleys has a greater effect on the passivation quality, comparing with the rounding of pyramid peaks.

Because rounding of peaks and valleys both improve the passivation quality, the combination of CP1 and CP2 was employed. The wafer was etched in CP1 solution for 4 minutes, subsequently etched in CP2 solution for 4 minutes. The SEM image is shown in Figure 1(B). It can be seen from the image that both pyramid peaks and valleys are rounded. The average reflectivity between 400 and 1100 nm is 12.46%, higher than that with 4 minutes CP1 etching or 4 minutes CP2 etching. After PECVD, the lifetime and implied Voc are tested to be 5147 μs and 0.747 V, respectively, much higher than those with 4 minutes CP1 etching or 4 minutes CP2 etching. The results confirm the additive effect of CP1 and CP2 etching on the passivation quality. CP1 etching rounds the valleys, whereas CP2 etching rounds the peaks. The combination of them produces a more suitable pyramid profile for a-Si:H deposition.

### 3.3 Electrical properties of SHJ cells

Silicon heterojunction cells were fabricated with three CP treatment conditions, the cells quantity was 50 for each condition. The first condition was etching in CP1 solution
for 4 minutes, the second was etching in CP2 solution for 4 minutes, and the third was etching in CP1 and CP2 solution in turn for respective 4 minutes. The electrical properties are listed in Table 2, and the corresponding scatter diagrams are shown in Figure 6. Cells with CP2 etching have a lower Voc than CP1, in agreement with the implied Voc (Figure 4(D)). Cells with CP1 + CP2 etching have higher Voc and FF than CP1 or CP2, resulting in a higher conversion efficiency of 23.18%. However, the reflectivity of CP1 + CP2 etched samples is higher than that of CP1 or CP2, weakening the light trapping, hence causing a lower Isc.

**TABLE 2** Electrical properties for SHJ solar cells with different CP treatment conditions. Each value is the average for 50 cells

| CP condition          | Isc (A) | Voc (V) | FF (%) | Eff (%) |
|-----------------------|--------|---------|--------|---------|
| CP1 (4 min)           | 9.250  | 0.742   | 81.95  | 23.02   |
| CP2 (4 min)           | 9.278  | 0.738   | 81.30  | 22.79   |
| CP1 (4 min) + CP2 (4 min) | 9.238  | 0.745   | 82.23  | 23.18   |

Another benefit of CP1 + CP2 etching can be seen in the scatter diagrams. The dispersion of Voc for CP1 + CP2 etched cells is much lower than that of CP1 or CP2, and so does the dispersion of conversion efficiency. The convergent distribution of electrical properties is very beneficial for industrial production. The controllability and stability of product quality can be improved greatly. The Voc and Eff for CP2 etched cells are widely scattered, which implies that the rounding of pyramid valleys is more beneficial than the rounding of pyramid peaks. A possible explanation could be that during the a-Si:H deposition process, the mass transfer in the narrow valleys is more difficult than on the peaks, therefore, defects are more likely to appear at the valleys. In conclusion, in order to acquire a good quality of a-Si:H layer, both peaks and valleys need to be rounded.

### 4 CONCLUSION

The effects on the pyramid profiles and cell performances using two CP etching solutions are investigated. The two
solutions CP1 and CP2 consist of 68% HNO₃ + 0.2% HF and 80 ppm O₃ + 0.8% HF, respectively. It was found that pyramid peaks and valleys can be rounded selectively in different CP solutions. CP1 etching rounds the pyramid valleys but not the peaks, whereas CP2 etching rounds the pyramid peaks but not the valleys. The different rounding effects might be originated from the different mass transfer mechanisms for the etching reactions. Both rounding of peaks and valleys improve the passivation quality of a-Si:H, and the combination of CP1 and CP2 etching generates a higher lifetime than each of them. The Voc, FF, and Eff for cells with the combined etching are also improved. It is worth noting that these cells are showing a good convergence for electrical properties distribution, which is very beneficial for industrial production.

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