19.31%-efficient multicrystalline silicon solar cells using MCCE black silicon technology

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ABSTRACT

A novel nanoscale pseudo-pit texture has been formed on the surface of a multicrystalline silicon (mc-Si) wafer by using a metal-catalysed chemical etching (MCCE) technique and an additional chemical treatment. A desirable nanoscale inverted-pyramid texture was created by optimizing the recipe of the MCCE solution and using a proprietary in-house chemical post-treatment; the depth and width of the inverted pyramid was adjustable within a 100–900nm range. MCCE black mc-Si solar cells with an average efficiency of 18.90% have been fabricated on CSI's industrial production line, equating to an efficiency gain of ~0.4%$_{abs.}$ at the cell level. A maximum cell efficiency of 19.31% was achieved.

Introduction

In most industrial production lines, the typical power conversion efficiencies η for single-crystalline silicon (sc-Si) and multicrystalline silicon (mc-Si) solar cells are over 19.5% and 18.5% respectively [1]. Cell performance has been improved by enhancing the electrical and optical properties, through higher-quality wafers, better passivation on the front and rear surfaces, more-effective light trapping via the interdigitated back contact and metal wrap-through, etc. [2–5].

In recent years mc-Si solar cells have been maintaining a firm hold on the leading position in the PV market. However, the higher light reflection at the front textured surface of mc-Si results in an η that is around 1–1.5% lower than that of sc-Si. In fact, the random pits or honeycomb texture formed on the surface of mc-Si via

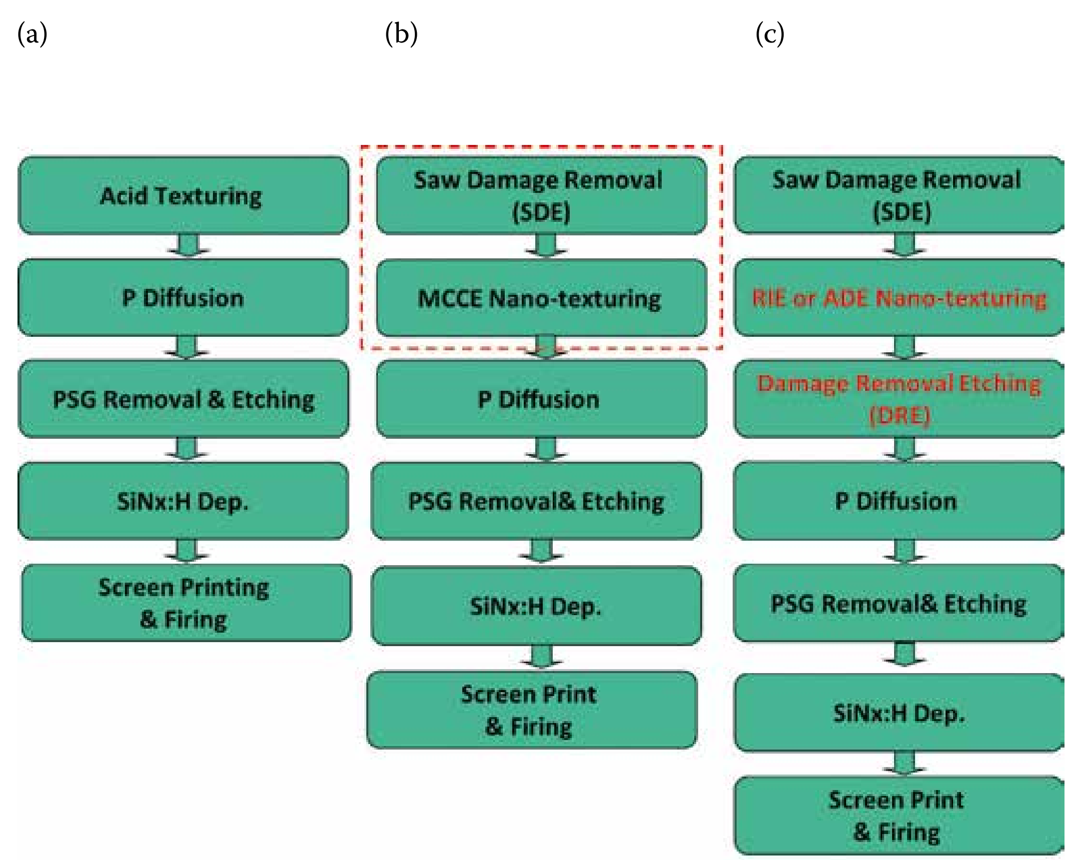

Figure 1. Process flow simplifications: (a) typical mc-Si solar cell; (b) MCCE black mc-Si solar cell; (c) RIE black mc-Si solar cell.

Cell (type, size)	Method	Passivation and ARC	R [%]	η [%]
mc-Si (p, 15.6×15.6cm^2)	RIE	PECVD-SiN_x	13.7	16.1 [10]
mc-Si (p, 15×15cm^2)	RIE	PECVD-SiN_x	N/A	17.1 [22]
sc-Si (n, 4cm^2)	RIE	ALD-Al_2O_3	1.9	18.7 [23]
sc-Si (p, 0.8081cm^2)	MCCE ($AgNO_3$)	Thermal oxide SiO_2	4.6	18.2 [20]
sc-Si (p, N/A)	MCCE ($AgNO_3$)	Al_2O_3	2.5	18.2 [24]
mc-Si (p, 4cm^2)	MCCE ($AgClO_4$)	PECVD-SiN_x	22	16.6 [25]

Table 1. State of the art of nanostructured Si solar cells.

isotropic acidic etching is not as effective at trapping light as the pyramid texture formed on an sc-Si wafer based on anisotropic alkali etching [6,7]. If more-effective light-trapping texture could be fabricated into mc-Si cells, there would be high potential for increasing η, and even surpassing 19%.

"Nanostructure textured black silicon is more effective at trapping light."

It is well known, and has been proved, that nanostructure textured black silicon is more effective at trapping light, and therefore demonstrates significant potential in application to silicon-based solar cells [8–10]. Several advantages of black silicon solar cells can be inferred:

- Excellent light trapping over a wide spectrum range (300–2,000nm) [11].
- Possibility of eliminating the expensive vacuum process of plasma-enhanced chemical vapour deposition (PECVD).
- Wider acceptance angle for incoming light [12].

There are three main techniques for fabricating black silicon: 1) laser texturing [8,13]; 2) reactive ion etching (RIE) [10,14–16]; and 3) metal-catalysed chemical etching (MCCE) [9,17–19]. For industrial production, the RIE and MCCE methods show the greatest promise.

Process flow and experiment

Fig. 1 shows the process flow simplifications for MCCE and RIE black mc-Si solar cells, compared with the process flow for a typical solar cell. Clearly, MCCE is much more suitable for current production lines, in which the conventional texturing process is also based on wet chemical etching.

Oh et al. reported an efficiency of 18.2% for black single-crystalline silicon (Bsc-Si) solar cells [20]. Although this efficiency is still lower than that currently achieved at the industrial level, it demonstrates that significant progress is being made in the MCCE technique. The reported efficiencies for black multicrystalline silicon (Bmc-Si) solar cells based on either RIE or MCCE, however, are still very low, namely 12–16.6%.

Table 1 summarizes the state of the art of black Si solar cells; the techniques listed are still at the laboratory stage and have not yet been implemented on an industrial scale. While nanostructured silicon can certainly absorb sunlight over a broad range of wavelengths and incidence angles, it also introduces more recombination centres and non-uniform doping into the cell [20,21]. A trade-off between optical gain and recombination loss must therefore be considered in order to achieve high efficiency.

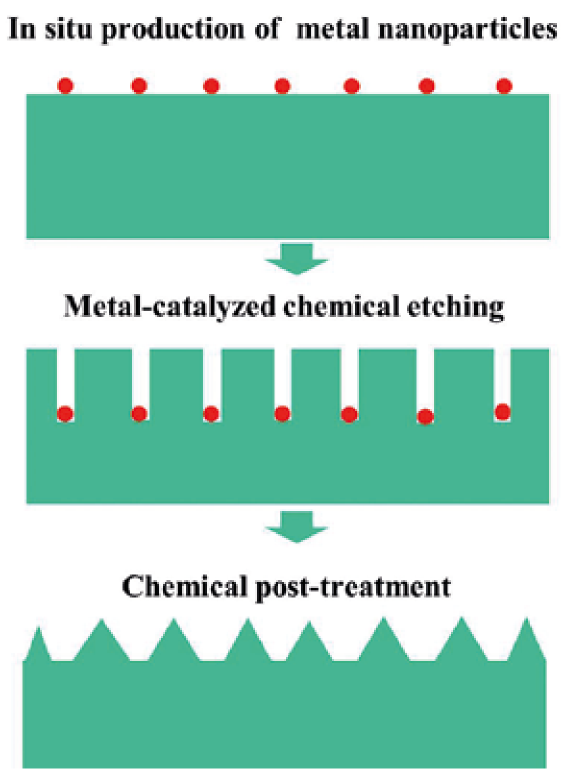

Figure 2. Main steps of the MCCE nanotexturing process.

This paper reports on the work carried out on the formation of a novel nanoscale pseudo-pit texture on the surface of an mc-Si wafer by using an MCCE technique and an additional chemical treatment. Fig. 2 illustrates the main steps of the MCCE nanotexturing process. In the first step, a noble metal (such as Au, Ag or Pt) is deposited on the Si surface, usually as nanoparticles (NPs). In the second step, a porous layer on the surface is formed by dipping the silicon substrate into a mixed aqueous solution of an oxidizing reagent (such as H_2O_2) and HF acid. Finally, to reduce the recombination due to a large surface area, the third step, i.e. chemical post-treatment, is crucial. In CSI's industrial production line, an average efficiency of 18.90% has been achieved, with the best-performing cell delivering 19.31% – the highest reported value so far for black silicon.

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Results and discussion

The nanoscale structures of different sizes and shapes are shown in Fig. 3. It was found that the morphology of nanoscale structures is highly dependent on the concentration of metal ions, the volume ratios of H_2O_2:HF:DIW (de-ionized water), the post-treatment chemicals, and the etching times of the above process steps.

In CSI's experiments, by adjusting the recipe of the MCCE solution and using a suitable alkali post-treatment it is possible to obtain a nanoscale pyramid or inverted-pyramid texture: for instance, a high Ag ion concentration results in a nanoscale *pyramid* texture, whereas a low Ag ion concentration leads to a nanoscale *inverted-pyramid* texture. When the recipe of the MCCE solution is adjusted and a proper acid post-treatment is employed, a nanoscale *pseudo-pit* texture can be created. If a particular type of processing is added after the metal NPs deposition, an orderly nanoscale *wormhole* texture will be formed.

A desirable nanoscale inverted-pyramid texture was created by optimizing the recipe of the MCCE solution and employing a proprietary in-house chemical post-treatment, as shown in Fig. 4. It was possible to adjust the depth and width of the inverted pyramid within a 100–900nm range. An appropriate size of inverted-

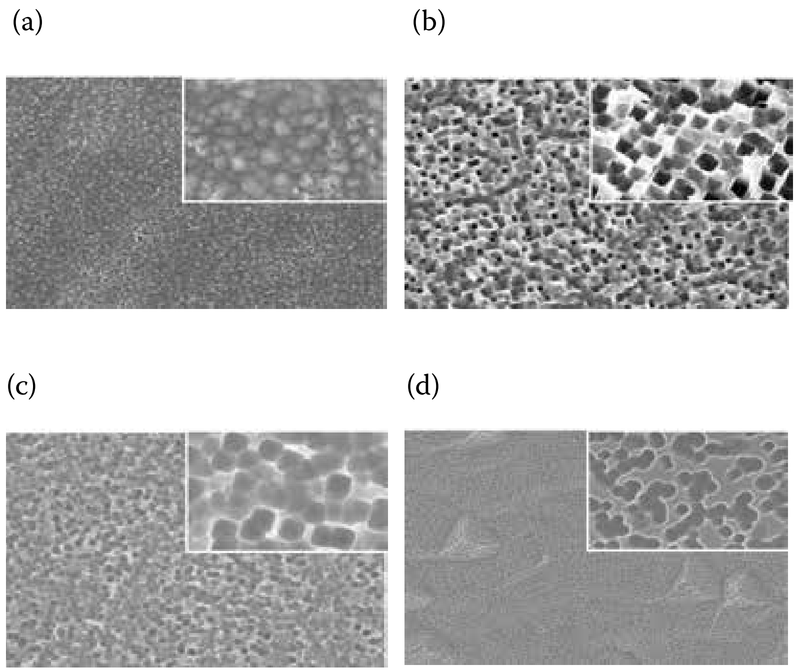

Figure 3. SEM surface images of nanoscale textures: (a) pyramid; (b) inverted-pyramid; (c) pseudo-pit; (d) wormhole.

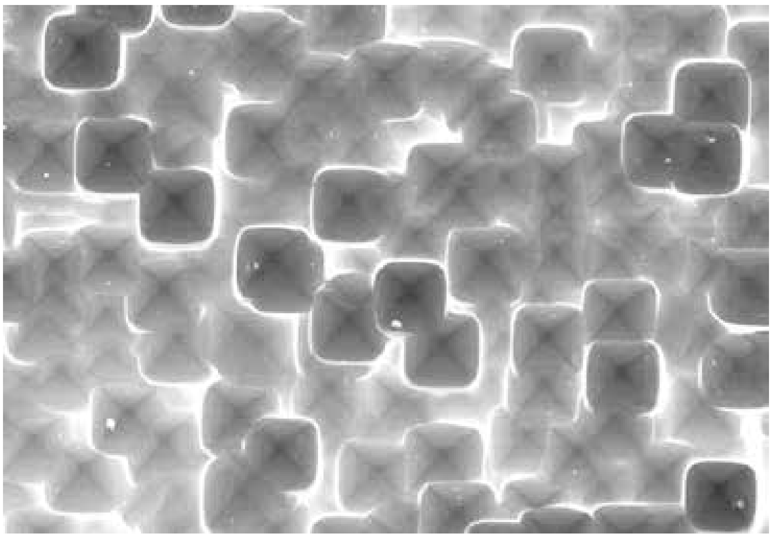

Figure 4. SEM image of a desirable nanoscale inverted-pyramid texture.

	V_{oc} [mV]	I_{sc} [A]	R_s [mΩ]	R_{sh} [mΩ]	FF [%]	EFF [%]
Baseline-Avg	637.6	8.842	1.80	506	79.90	18.51
MCCE-Avg	638.6	8.981	1.70	607	80.19	18.90
Best cell	642.4	9.109	1.68	599	80.31	19.31

Table 2. Main characteristics of mass-produced MCCE black mc-Si and typical mc-Si solar cells (baseline).

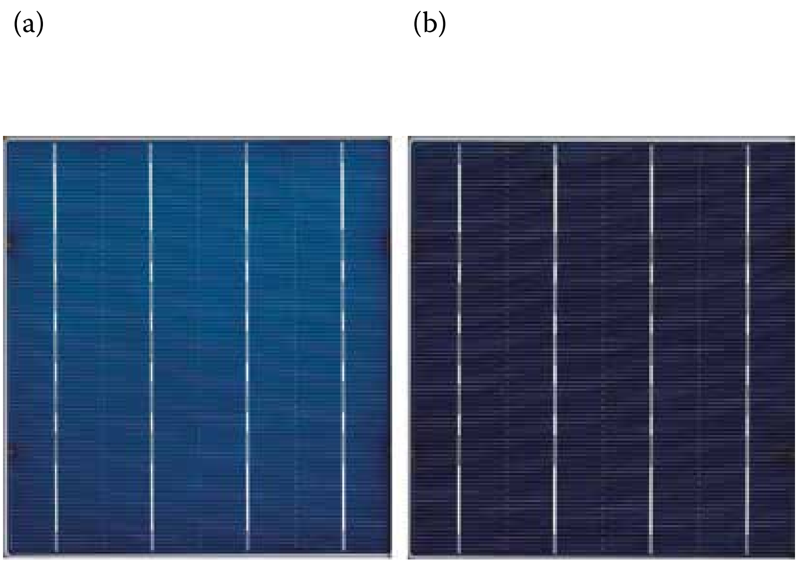

Figure 5. Cell photographs: (a) typical mc-Si solar cell; (b) MCCE black mc-Si solar cell.

pyramid texture can ensure a reduced surface recombination, while keeping the reflectance low.

With the above-mentioned optimization of the nanoscale structure texture, the average efficiency of mass-produced MCCE black mc-Si solar cells was 18.90%, while the typical mc-Si cells (the baseline) yielded 18.51%; this equates to an efficiency gain of ~0.4% at the cell level.

The mean parameters of the black cells are summarized in Table 2. As expected, the short-circuit current shows an increase of around 140mA, which can be mainly attributed to the enhanced light absorption of the cells. The average open-circuit voltage V_{oc} of MCCE black mc-Si solar cells is approximately 1.0mV higher than that of the baseline, thanks to the low J_{02} value of MCCE cells. On the basis of a two-diode model, the J_{02} accounts for the injection-dependent Shockley-Read-Hall recombination in the space charge region; moreover, such low injection recombination can be attributed to a flat p-n junction after MCCE texturing. Indeed, the average fill factor FF of MCCE black mc-Si solar cells is around 0.3% higher than the baseline.

Compared with the light-blue appearance of a typical mc-Si solar cell, the appearance of an MCCE mc-Si solar cell is dark blue, as shown in Fig. 5. The grains of an MCCE mc-Si solar cell, however, are more perceptible than in the case of a typical acid-textured solar cell, because of the different reaction rates of the grains in the random crystalline orientation in MCCE cells.

"There is still significant potential for improvement of the efficiency of MCCE black mc-Si cells through an effective passivation technique and further optimization of the MCCE process."

Conclusions

MCCE is a more economical and efficient approach for industrial black mc-Si manufacturing. A desirable nanoscale structure can be made by adjusting the recipe of the MCCE solution and using a proprietary in-house chemical post-treatment processing, which will ensure a trade-off between optical gain and recombination in order to achieve high efficiency. The conversion efficiency achieved at CSI of mass-produced MCCE black mc-Si solar cells was ~18.90%, which equated to an efficiency gain of ~0.4%$_{abs.}$ at the cell level; the efficiency of the best-performing cell was 19.31%. There is still significant potential for improvement of the efficiency of MCCE black mc-Si cells through an effective passivation technique and further optimization of the MCCE process. Moreover, the authors believe that MCCE is an ideal technique for solving texturing problems with diamond-wire-sawn mc-Si wafers and direct wafers.

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