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Black multi-crystalline silicon solar cells

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A simple method for nano-scale texturing of silicon surfaces based on local metal-catalyzed wet chemical etching, which results in an almost complete suppression of reflectivity in a broad spectral range, has been successfully applied to produce black multi-crystalline silicon solar cells. The performance of the cells is compared to that of reference cells without surface nano-texturing. A considerable increase of the short circuit current (by 36–42% with respect to the reference cells) without deterioration of other performance parameters is observed under natural sun illumination. Means of further optimization of such black solar cells are discussed.

Introduction The performance of solar cells depends critically on the optical losses caused by the high semiconductor reflectivity. The efficiency of single crystalline silicon solar cells can be increased by deeply textured surfaces (structure depth of several micrometers), which appear black due to a strong reduction of reflectivity in a broad spectral range [1]. This kind of texturing based on anisotropic KOH etching is applicable only to (100) oriented single crystalline silicon. The development of highly efficient solar cells using cost-effective materials (multi-crystalline, ribbon, or thin film Si) requires other techniques to reduce the reflection losses. Up to now, these kinds of solar cells mainly utilize interference antireflection coatings (ARC). However, simple ARC's based on quarter-wavelength layers perform well in a limited spectral range and for a certain angle of light incidence only. Alternatively, isotropic texturing methods based on acidic solutions containing HF, HNO_3 and additives [2, 3] develop the saw damage of wafers and result in the formation of randomly overlapping hemispherical pits of submicrometer size on the surface of microcrystalline Si. On its own, this kind of texture reduces the average Si reflectivity to 10–17%. When used in combination with an additional ARC, the reflectivity is generally further reduced to 3–6%.

Recently, we have developed a simple method for the nano-scale texturing of silicon surfaces, which results in an almost complete suppression of reflectivity in a broad spectral range [4]. The texture consists of peaks and pits with lateral sizes of 50–150 nm and penetrates only about 300 nm into the Si surface. Its optical effect originates from the smooth variation of the optical constants across the effective medium of the air/Si boundary layer [5]. The texturing method, referred to as “black Si etching”, employs a metal-catalyzed wet chemical process, which is independent of the crystallographic orientation and doping [4]. Thus, it is applicable to large area silicon substrates of different microstructure (single-, poly-, microcrystalline, or amorphous) and therefore is appealing for the production of a variety of solar cells. In this letter, we demonstrate that the application of the nano-scale texturing is indeed beneficial to the performance of multi- and tri-crystalline Si solar cells. The delicate nano-texture survives the harsh chemical and thermal treatments during solar cell processing. Furthermore, no negative influences of the new texturing process, which includes the temporary use of Au, on the electronic properties of the solar cells were observed. To incorporate the nano-textured Si surfaces into the solar cells, we first texture the source material by black etching and then fabricate a solar cell from this black Si substrate following standard technology. Simultaneously, a reference cell is produced in the same way directly from the raw material without black etching.

Two kinds of source material have been used: (i) multi-crystalline Si wafers (p-type, specific resistance $\rho = 0.85\ \Omega$ cm) and (ii) tri-crystalline Si wafers [6] (p-type, $\rho = 3.6\ \Omega$ cm). They are referred to below as “mc-Si” and “tri-Si”, respectively. Both sorts of wafers were supplied without removal of the saw damage and with a typical grainy surface. The wafers were first mechanically cut into square pieces of 22 × 22 mm^2 size. Subsequently, the following process steps were performed. Note that the entire process has not yet been optimised for these materials.

Pre-cleaning and removal of the saw damage All samples were first degreased by acetone and iso-propyl-alcohol and then cleaned from organic residua by "Piranha etch", followed by immersion in diluted HF (5 wt% HF, 2 min). Then, 8–10 µm of material from the saw-damaged front and back surfaces was removed by an isotropic chemical polishing ($HNO_3:HF:CH_3COOH = 5:1:1$) at room temperature for 45–60 s. This results also in a smoothing of the grainy surface structure, which is favourable for the next step. The process is completed by washing in deionized water and drying in N_2.

Black etching To obtain a nano-structured black surface, a thin layer of gold with a nominal thickness of 0.7–1 nm was deposited on the surfaces by thermal Au evaporation. Such a layer is discontinuous and nearly invisible and consists of nano-size Au islands. After removal from the evaporation system, the samples were etched in $HF:H_2O_2:H_2O = 1:5:10$ at room temperature for 2 min. Due to the local catalytic action of the Au clusters, this treatment results in the nano-scale texturing described above. Then, the Au is removed by etching in $I:KI:H_2O = 1:4:40$ for 2 min. After this step, no Au can be detected on the black surface by XPS measurements (sensitivity ~1% of a monolayer).

Since Au is a detrimental impurity in Si, we subsequently applied also a standard SC2 clean ($HCl:H_2O_2:H_2O = 1:1:6$, 80 °C, 15 min) to further reduce (or completely remove) an eventual metal residue. As can be seen in Fig. 1, the resulting texture leads to a strong reduction of the reflectivity with a simultaneous improvement of light coupling to the Si bulk [4].

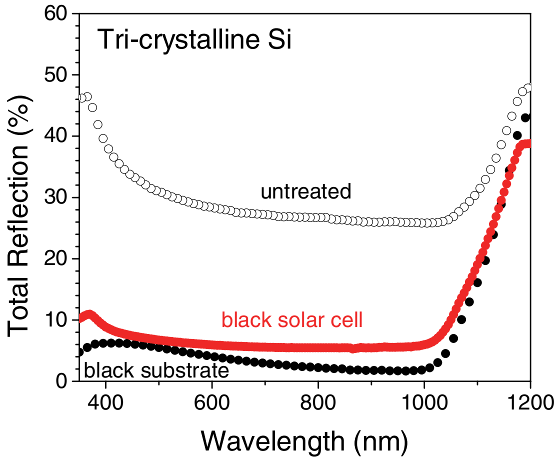

Figure 1 (online colour at: www.pss-rapid.com) Total hemispherical reflection spectra of tri-crystalline Si measured at different stages of the solar cell fabrication: initial (untreated) substrate, substrate after texturing with black etching and black solar cell after completion of all high-temperature processing steps. The spectra are shown in the region of strong Si absorption. The corresponding spectra of the mc-Si samples (not shown) are almost identical.

Formation of emitter The emitter of all cells was formed by diffusion of Phosphorus from a spin-on dopant through the front surfaces (black-etched or untreated). A uniform film of solid doping source (P509, Filmtronics, USA) was spun on at 3000 turns/min for 11 sec and cured at 200 °C for 10 min. The indiffusion was performed in an atmosphere of 25% O_2 and 75% N_2 in a closed quartz tube mounted in an oven. The tri-Si cells were processed at 900 °C for 71 min, while the mc-Si samples were processed for the same time, but at 930 °C in order to obtain higher doping. The doping source was removed from all samples by etching in concentrated HF (50%). The diffusion resulted in the formation of n-type regions below the front surfaces with respective sheet resistances of 38 Ω/sq. (reference tri-Si sample), 76 Ω/sq. (black tri-Si) and 20 Ω/sq. (reference mc-Si), 31 Ω/sq. (black mc-Si).

Surface passivation The surfaces of all samples were oxidized in dry O_2 at 840 °C for 30 min, followed by annealing in N_2 at the same temperature for 15 min. This treatment results in the formation of about 10 nm of conformal dry oxide layer with an annealed interface to the Si, intended to reduce the surface recombination at the heavily doped emitters. After performing the high temperature steps, a slight change of front surface reflectivity can be detected as shown in Fig. 1.

Formation of back contact The passivating oxide was removed from the back surface of all samples by an HF dip (5%, 2 min) and a 50 nm thick Al and a 600 nm thick Ag layer were deposited on these surfaces by vacuum evaporation. The contacts were annealed first at 600 °C (above the Al/Si eutectic temperature) for 15 minutes and then at 550 °C (below the eutectic temperature) for 20 min. The purpose of this treatment is to reduce the contact resistance and recombination by Al/Si alloying and p^+-type doping of the rear-contact region. Finally, the edges of all samples were mechanically ground to form squares of 20 × 20 mm^2 area, thus removing eventual short circuit paths due to edge junctions or metal bridges between the front and the rear surfaces.

Formation of front contact grid An array of slits – 50 µm wide, parallel to one side of the cell and separated by 2 mm pitch – was opened in the passivating oxide on the front surfaces of all samples by photolithographic patterning and HF etching. The slits were covered by a 50 nm thick Ti layer using vacuum evaporation and lift-off of photoresist. Grids of wider Ag contact fingers (170–200 µm) with an interconnecting bar (1 mm wide) were deposited over the Ti strips by vacuum evaporation through shadow masks. This geometry resulted in 11% to 14% shadowing of the front surfaces. The front contacts have not been annealed.

Solar cell performance Figure 1 clearly shows the dramatic reduction of reflectivity after the formation of the textured surface (black substrate without additional ARC). On the other hand, the high temperature processing steps during the solar cell formation result in a slight recovery of

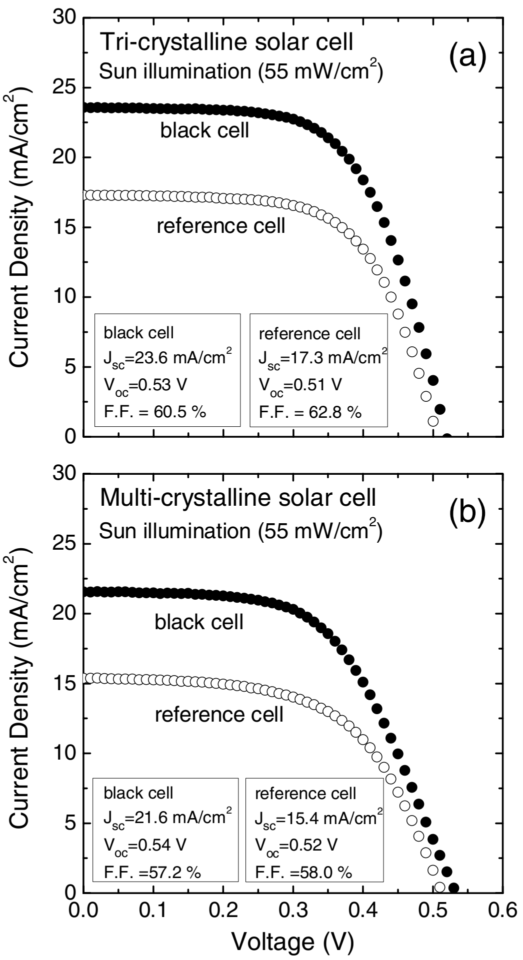

Figure 2 Current–Voltage characteristics under natural sun illumination with an intensity of 55 mW/cm^2 of (a) a black tri-crystalline Si solar cell with nano-textured front surface in comparison with a reference tri-crystalline Si solar cell with untreated surface; (b) a black multi-crystalline Si solar cell (nano-textured) in comparison with a reference multi-crystalline Si solar cell (untreated). The labels show the respective solar cell performance parameters – short circuit current density J_{SC}, open circuit voltage V_{OC}, and fill factor F.F. The efficiencies of the black cells can be estimated to be in the 12–14% range.

the reflectivity. Nevertheless, the reflectivity remains at quite reasonable values of about 6% on average, which should result in an increase of the total absorption of the incident light within the Si bulk by about 34% with respect to a sample without an anti-reflection treatment.

Figure 2 shows the current–voltage characteristics of the solar cells made from tri-Si and mc-Si under sun illumination conditions. It can be seen that the major difference between the black and the reference cells in both cases is a significant increase of the photocurrent of the black textured cells by about 36–42% with respect to the reference cells. This effect is even slightly larger than expected, considering the increase of the average optical absorption by about 35% as discussed above. Thus, one can conclude that the black etching treatment does not have a detrimental effect on the solar cell, despite of the temporary use of gold. This conclusion is supported by the fact that the other performance parameters (open circuit voltage and fill factor) are nearly the same for the black and the reference samples. The modest values of these parameters can be explained by general imperfections of the non-optimized solar cell manufacturing used in this preliminary work.

It is interesting to compare the effects of different means for the minimization of the optical losses on the photocurrent enhancement of multi-crystalline-Si solar cells. The use of common antireflection coatings often results in a typical increase of about 20–30% of the short circuit current J_{SC} with respect to untreated cells. The effect of nano-structured surfaces demonstrated in this work, reaches current enhancements of about 40%. Thus, one can conclude that the black surface texturing is beneficial compared to conventional ARC's. Still, a further optimization of the solar cell fabrication making better use of the black nano-texture can be expected. In particular, the use of spin-on dopant leads to a smoothening of the nanotexture, which promotes the reflectivity again. Alternatively using gaseous dopant sources could circumvent this problem. Furthermore, the black-etched cells could benefit from an optimized deeper emitter. This is related to the fact that the heavily doped region coincides with the textured layer, allowing in principle a thicker emitter with improved electrical properties but reduced absorption.

Conclusion We have shown that the black nano-textured surface formed by local metal-catalyzed wet chemical etching is compatible with the common technological processes used in solar cell production. Its positive optical effect reasonably survives the harsh treatment associated with these processes. In addition, the black etching process (despite the temporary exposure of the surface of the source material to Au at room temperature) and the nano-textured surface itself do not show negative influences on the quality of the solar cells. Rather, the application of the black nano-texture significantly improves the solar cell photocurrent and does not influence other performance parameters. The method therefore can be of interest especially to increase the efficiency of solar cells made of cost-effective materials.

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