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17.1%-Efficient Multi-Scale-Textured Black Silicon Solar Cells without Dielectric Antireflection Coating

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ABSTRACT

In this work we present 17.1%-efficient p-type single crystal Si solar cells with a multi-scale-textured surface and *no* dielectric antireflection coating. Multi-scale texturing is achieved by a gold-nanoparticle-assisted nanoporous etch after conventional micron scale KOH-based pyramid texturing (pyramid black etching). By incorporating geometric enhancement of antireflection, this multi-scale texturing reduces the nanoporosity depth required to make silicon 'black' compared to nanoporous planar surfaces. As a result, it improves short-wavelength spectral response (blue response), previously one of the major limiting factors in 'black-Si' solar cells. With multi-scale texturing, the spectrum-weighted average reflectance from 350- to 1000-nm wavelength is below 2% with a 100-nm deep nanoporous layer. In comparison, roughly 250-nm deep nanopores are needed to achieve similar reflectance on planar surface. Here, we characterize surface morphology, reflectivity and solar cell performance for the multi-scale textured solar cells.

INTRODUCTION

While dielectric antireflection (AR) coatings remain the photovoltaic industry standard, many alternative approaches to achieve AR in Si for photovoltaic and other optoelectronic applications are being explored by research groups [1]. Some of these approaches include anodic electrochemical etch [2], metal-assisted etch [3], dry plasma etch [4] and laser-induced etching [5]. Our group at NREL has previously demonstrated a 16.8%-efficient Si solar cell with Au nanoparticle-assisted black Si AR layer in place of the conventional quarter-wavelength SiN_x AR coating [6,7]. The black Si layer is made by a one-step liquid etch and would eliminate a vacuum-coating step from the Si solar cell production. The physics of nanostructured black Si AR is based on the existence of a graded index of refraction: if the nanostructure is comprised of structures smaller than the wavelength of incident light and the Si density is graded across a thickness more than about half the wavelength of light, reflection is strongly suppressed [8]. The black Si provides broader band and wider angle-of-view AR than quarter-wavelength interference coatings [9]. However, blue response in the black Si cells is poor, due to high recombination in the nanoporous surface layer [7]. One of the major suspects for high recombination is the high surface area of the nanoporous structure. Unfortunately, as mentioned previously, a good AR puts stringent requirements on both feature size and the depth of the nanostructure and inevitably results in high surface area. By combining the nanostructured black Si layer with a conventional micron-scale KOH-etched pyramidal texture as a multi-scale texture, we can reduce the amount of surface area required to achieve good AR properties. The reason is that micron-scale pyramidal texture enhances AR in a purely geometric optics effect; some of the reflected light is incident on neighboring pyramids for a second chance of absorption. So even though nanostructured black Si must still have feature sizes smaller than the wavelength of light, when combined with pyramid texture its depth can be greatly reduced. Our study found pyramid texture with nanostructures only 100-nm deep provides reflectivity below 2% across a wavelength range of 350-1000 nm. In comparison, nanostructures roughly 250-nm deep are needed to achieve similar reflectance on a planar surface where pyramid texture is absent. With the reduced nanostructure depth (and surface area) we have achieved a conversion efficiency of 17.1% on a multi-scale textured black Si solar cell that exhibits improved blue response and higher short-current density (J_{sc}) compared to our best planar black Si cell.

MULTI-SCALE TEXTURED BLACK SI SURFACE FORMATION

We first perform conventional alkaline etch and then the one-step black Si etch to create multi-scale textured surface. A p-type c-Si (100) FZ wafer with resistivity of 2.7 Ω-cm and thickness of 300 μm is immersed in 10% HF for 1 min to remove any native oxide. Then, we perform pyramidal texturing of both faces in a 600-ml solution of 2.5% KOH in deionized (DI) water with 200-ml isopropanol and bubbling N_2 [10] for 25 min at 80° C. The textured wafer is then decontaminated from potassium impurities in $HCl:H_2O_2:H_2O$ 1:1:5 mixture at 80° C for 10 min [11]. Next, a one-step black etch is performed on the front side of the substrate (back side protected with paraffin) by immersing the pyramidal textured Si wafer in 0.4-mM $HAuCl_4$ solution and adding an equal quantity of $HF:H_2O_2:H_2O$ 1:5:2 mixture in a sonication bath. After the black etch, residual Au impurities are removed by immersing the wafer in I_2/KI solution. Finally, the protective paraffin is removed using an organic solvent.

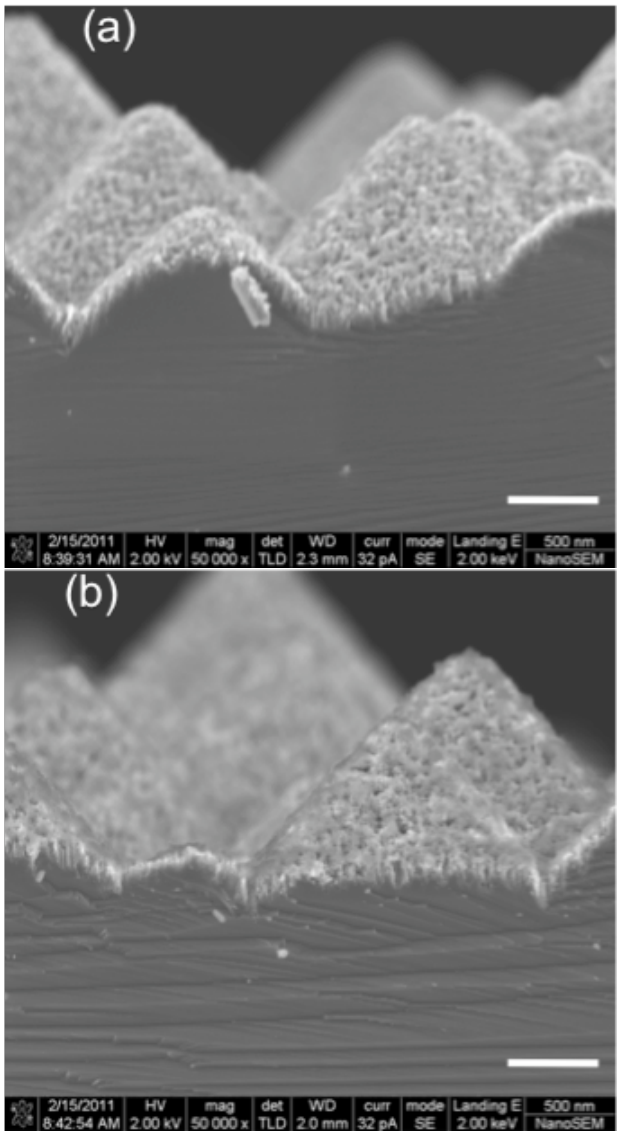

Fig. 1. Cross-sectional SEM images of as-etched multi-scale textured Si with (a) 1.5-min and (b) 3-min Au-assisted black etch. Magnification on both images is identical and the white scale bar represents 500 nm.

Multi-scale textured samples were prepared for various black etch times from 1 min to 3 min. Figure 1 shows the cross-sectional SEMs of two representative multi-scale textured samples with 1.5- and 3-min black etch time. The vertical nanopores are along the [100] direction even though the exposed pyramid facets are {111}. Thus, the pore structure on pyramidal textured black Si is similar to black Si etched into the planar (100) surface shown in [7].

SOLAR CELL FABRICATION AND ITS EFFECTS ON NANOPOROUS LAYER MORPHOLOGY

We clean the multi-scale textured black Si substrates with RCA-1, 10% HF and RCA-2 to remove any organic and inorganic contaminants. The substrates are then processed with one-step $POCl_3$ and dry thermal oxidation to obtain a diffused emitter and surface passivation layer in one tube furnace run. The emitter sheet resistance is 75 Ω/□ on a planar witness sample. The combined oxide and phosphosilicate glass (PSG) thickness measured by an ellipsometer on the planar witness wafer is 470 Å. After removing the backside oxide layer with dilute HF, Al paste is applied on the back followed by 800° C alloying for 5 min in a tube furnace to form the back-surface field. A front grid is then formed by chemically removing the oxide and PSG layer through a photolithographically defined photoresist pattern, e-beam evaporating metal (50/60/1000/100 nm Ti/Pd/Ag/Pd), and metal lift-off. Finally, 1x1-cm^2 cells are defined by photolithography followed by plasma etching to remove the exposed emitter and isolate the cells.

Previous studies on planar Si (100) surfaces [7,8] have shown that the pore depth of the as-etched nanostructure, d_E, is directly proportional to black etch time. However during the solar cell processing steps such as $POCl_3$ diffusion and oxidation the depth of the nanostructured porous layer is reduced such that the processed solar cell nanostructure depth, d_{SC}, is about two-thirds of d_E. This decrease in the nanoporous layer depth is mainly due to the consumption of Si during thermal oxidation. The remaining height of Si nanostructures (d_{SC}) may vary from pore to pore since the starting nanostructure feature size varies and oxidation consumes Si from all sides of the nanostructure. The result is the variations of pore width and depth (d_{SC}) as depicted in the schematic of Figure 2.

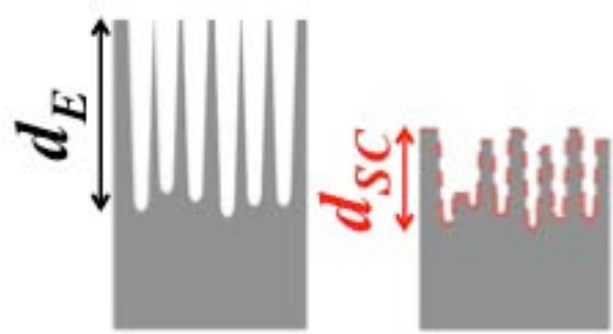

Fig. 2. Schematic depicting the effect of solar cell processing on nanoporous Si layer for as-black-etched, d_E, (square) and processed solar cell, d_{SC}, (circle).

PLANAR AND PYRAMID-TEXTURED BLACK SILICON OPTICAL CHARACTERISTICS

The goal of combining nanostructured black Si with micron-scale pyramid texture is to utilize geometric optics of of pyramids to obtain low reflectivity with a shallow nanostructure surface layer. We processed both planar and pyramid textured Si with various black etch times to compare the reflection and absorption. The reflection and transmission of the black etched Si are measured after the one-step emitter and passivation formation by a spectrophotometer (Varian, Cary 6000i) with an integrating sphere. Figure 3 shows the measured results at 400 nm and 1000 nm wavelengths. Absorption is calculated by subtracting reflection (%) and transmission (%) values from 100%.

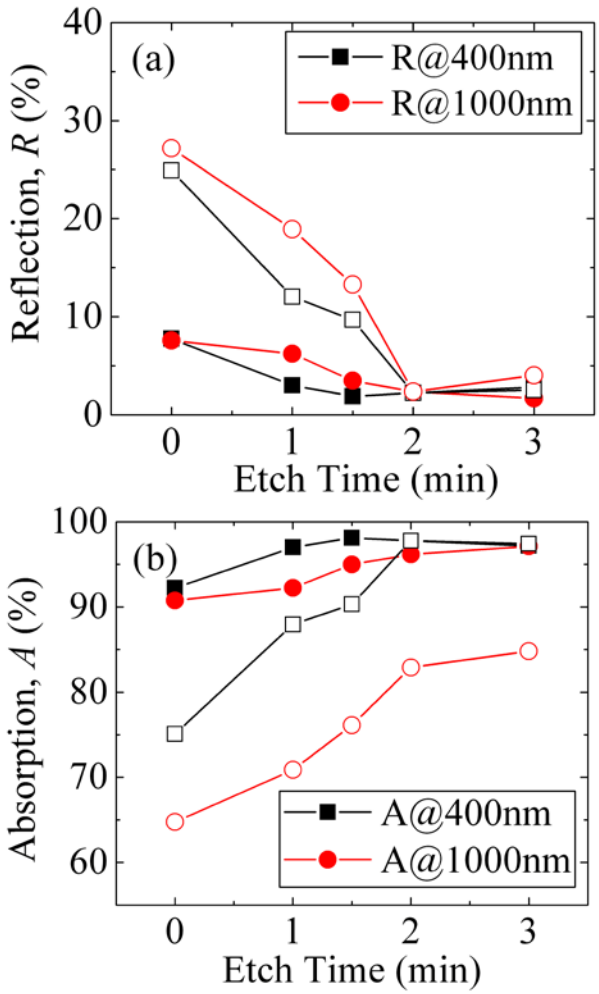

Fig. 3. (a) Reflection and (b) absorption of processed pyramid (solid symbols) and planar (open symbols) Si at 400 nm and 1000 nm after different black etch (BE) times. The 0-min BE planar sample refers to two-sided polished Si and the 0-min BE pyramid refers to two-sided pyramidal textured Si without any BE.

We calculate spectrum-weighted average reflection (R_{ave}) between 350- and 1000-nm wavelengths from the measured reflection spectra. The 1.5- and 2-min black-etched planar samples have R_{ave} of 6.9% and 2.7%, respectively. In comparison, black-etched pyramid Si etched for the same times have very low R_{ave} of 1.8% and 1.4%, respectively. So it is clear that geometric optics effect from pyramid texture enhances AR and enables short black etch time. Moreover, the absorption data of Figure 3(b) shows that the pyramidal textured black Si has higher absorption at the 1000 nm wavelength range due to the light-trapping effect of the random pyramids. This increased absorption in the near-IR can provide additional J_{sc} gain especially in thin film solar cells.

Hence a 1.5-min black etched multi-scale textured Si has R_{ave} of 1.8% with an extremely shallow pore depth of about 100 nm. In comparison, the pore depth needs to be about 250 nm on planar Si to achieve similar AR. Therefore multi-scale texture provides low reflection for high short-circuit current density (J_{sc}) with a nanoporous layer only around 100 nm deep.

HIGHER J_{SC} AND IMPROVED BLUE RESPONSE OF MULTI-SCALE TEXTURED BLACK SI SOLAR CELLS

Our previous 16.8%-efficient black Si solar cell [7] was a 3-min black etched cell on planar Si and processed using separated $POCl_3$ and oxidation steps where PSG was removed from the cell surface before thermal oxidation. R_{ave} for that cell was ~3% with J_{sc} of 34.1 mA/cm^2, open-circuit voltage (V_{oc}) of 612 mV and Fill Factor (*FF*) of 80.6%. Our best cell with the multi-scale texturing requires only a 1.5-min black etch on pyramidal textured Si to achieve R_{ave} of 1.8% and it has an independently confirmed conversion efficiency of 17.1%, J_{sc} of 35.6 mA/cm^2, V_{oc} of 615 mV, and *FF* of 78.2%. Figure 4 compares the illuminated AM1.5 current density-voltage (J-V) curves of our best multi-textured black Si solar cell and of the planar black Si cell. We attribute the 1.5-mA/cm^2 increase of J_{sc} in the multi-scale textured cell to a combination of lower R_{ave} and better blue response, as explained below.

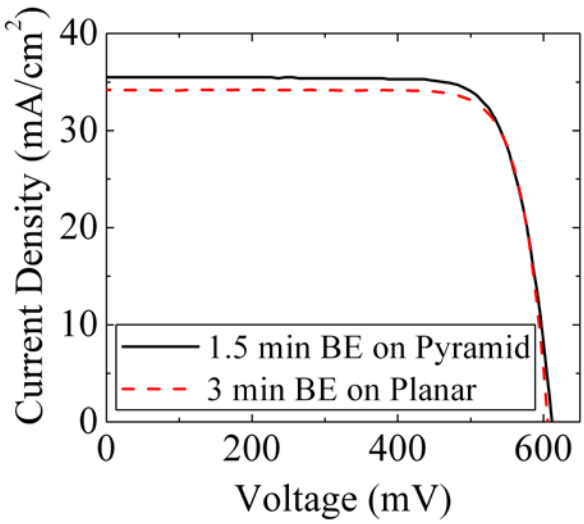

Fig. 4. Illuminated current density-voltage curves for 1.5-min black etched (BE) pyramidal textured Si (solid) and 3-min black etched (BE) planar Si (dashed) solar cells under 1-sun condition.

Figure 5 (a) shows improved blue response of the multi-scale textured cell in the internal quantum efficiency (IQE). Furthermore, the ratio of external quantum efficiency (EQE) spectra for 1.5-min black etched pyramid Si to 3-min black etched planar cell in Figure 5(b) shows that the blue EQE between 400-450 nm is enhanced by a factor of about 1.5. This improvement in blue response contributes to higher J_{sc} and is most likely related to the shallower nanopore depth. Further improvement in the blue response will be possible if surface passivation can be improved or surface area can be further reduced. Figure 5 (b) also shows a small improvement of EQE, around 10% in the near-IR (1000-1200 nm) for the multi-scale textured cell, which can be attributed to the improved light trapping of pyramid texture.

In conclusion, we have fabricated a 17.1%-efficient multi-scale textured solar cell without any vacuum-deposited dielectric AR coating. Instead, the AR is achieved by combining the advantages of geometric optics from micron-scale pyramid texture and of a density graded nanoporous black Si layer. We achieve R_{ave} of 1.8% with a nanoporous layer merely 100-nm thick on this multi-scale textured cell. Blue response is improved by about 1.5 times with the reduced nanopore depth and hence lower front-surface recombination. Our results suggest that most high efficiency nanostructured solar cells will be limited in efficiency by high surface recombination due to their high surface areas, and will therefore benefit from incorporation of light management strategies that minimize the nanostructured surface area without eliminating the benefits.

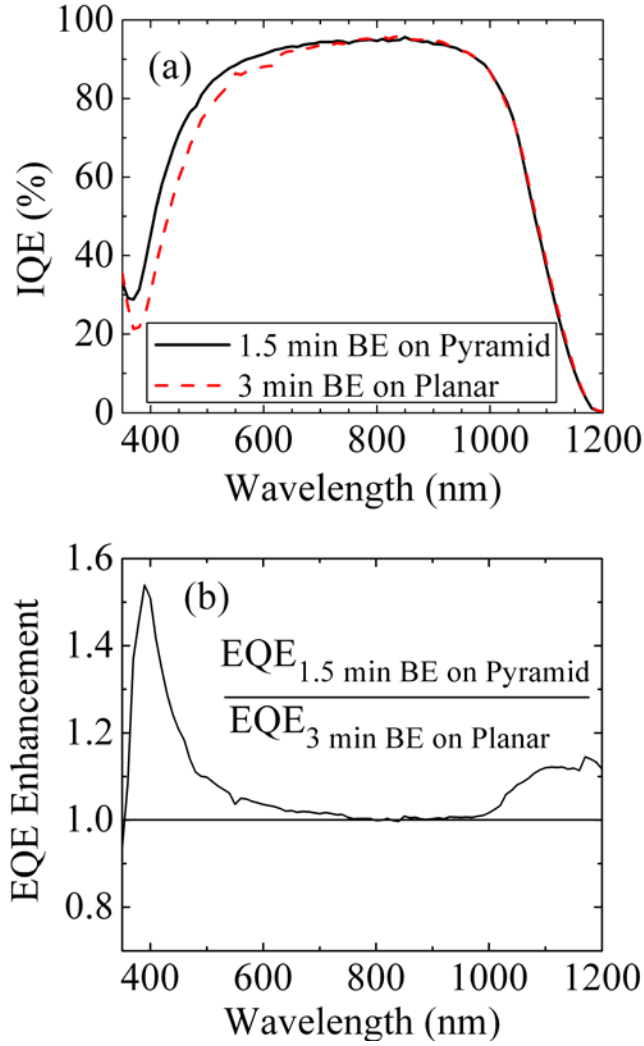

Fig. 5. (a) Internal quantum efficiency (IQE) and (b) external quantum efficiency (EQE) enhancement spectra as a function of wavelength for 1.5 min black etched (BE) pyramidal textured Si (solid) and 3 min black etched (BE) planar Si (dashed) solar cells.

ACKNOWLEDGEMENT

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