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Enhanced performance of solar cells with optimized surface recombination and efficient photon capturing via anisotropic-etching of black silicon

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We report an enhanced conversion efficiency of femtosecond-laser treated silicon solar cells by surface modification of anisotropic-etching. The etching improves minority carrier lifetime inside modified black silicon area substantially; moreover, after the etching, an inverted pyramids/upright pyramids mixed texture surface is obtained, which shows better photon capturing capability than that of conventional pyramid texture. Combing of these two merits, the reformed solar cells show higher conversion efficiency than that of conventional pyramid textured cells. This work presents a way for fabricating high performance silicon solar cells, which can be easily applied to mass-production. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4878096]

Enhancing light absorption is one of the most effective ways for improving conversion efficiency (CE) of silicon solar cells, because the reflectance of untreated silicon surface is really high. To reduce reflection, industrial solution is to chemically texture silicon surface followed by a deposition of SiN_x anti-reflection layer. However, conventional texture ways are hard to reduce the wafer reflectance below 10% in visible spectrum region, which may cause great power loss because the solar radiation mainly concentrates in 400–600 nm range.

To increase light absorption, several kinds of black silicon (BS) are applied to fabricate solar cells. Among them, the highest CE of 18.7% (Ref. 1) and 18.2% (Refs. 2 and 3) are reported recently, in which the BS surface are fabricated by reactive ion etching[1] (RIE) and metal-catalyzed-etching[2,3] method. In this work, we use femtosecond-laser treated black silicon (FS-BS) to fabricate solar cells, which mainly has two merits comparing with the record cells: First, formation of FS-BS surface can avoid Au or Ag contamination during process. Second, as fabricated FS-BS shows more efficient light-absorption properties over wide range solar spectrum.[4–6]

Since FS-BS was found in 1998,[7] there have been wide investigations on its formation mechanism,[8–10] below-band-gap absorption,[4–6] insulation to metal phase transition,[11] infrared photo detector application,[4,12] etc. However, laser-induced defects existed on the spike surfaces limit its wide applications.[13,14] These defects will become recombination centers to trap photon generated carriers, which result in low conversion efficiency, ranging from 1.2% to 7%.[15–17] To solve this problem, Nayak *et al.*[18] introduced a two-step etching procedure to remove it. Although an improved cell efficiency of 14.2% was obtained, a low open circuit voltage (V_{oc}) of 507 mV demonstrates a heavy surface recombination.

In this work, in order to obtain higher CE of solar cells based on FS-BS surface, we focus on the surface modification of FS-BS by removing laser-induced defects. First, a simple one-step anisotropic-etching is used to etch FS-BS for different time, and the corresponding morphology evolution is investigated; second, both surface recombination and light trapping properties of modified FS-BS surface are characterized; finally, the cell performance is investigated. Although modified FS-BS surface does not have sub-band-gap absorption properties any more, there are still some advantages after etching as follows: (1) Minority carrier life time of modified FS-BS surface increases substantially, which leads to an improved V_{oc} of 590 mV; (2) a surface of inverted pyramids/upright pyramids mixed texture (MT) is obtained, which shows better photon capturing ability over conventional pyramid textured (PT) surface, leading to a higher J_{sc} in solar cell performance. Combining these two merits, the CE of solar cells with modified FS-BS surface improves from 14.2% to 15.6%, which is higher than that of PT reference cells with efficiency of 15.3%.

In the experiments, 180 μm-thick boron-doped *p*-type single crystal silicon (100) wafers were used as the substrates, with a resistivity of 1.6 Ω·cm and bulk minority carrier life time in range of 20–25 μs. Saw damages were removed by immersing the wafers in 20 wt. %, 80 °C NaOH solution for 5 min, followed by a standard RCA cleaning. For black silicon fabrication, the silicon wafers were put in a chamber filled with SF_6 ambient under a pressure of 7×10^4 Pa for laser fabrication. A 11×11 mm^2 micro-structured black silicon was obtained by scanning the laser beam across the wafer with a laser wavelength of 800 nm and a pulse width of 130 fs. The laser fluence was 1.82 kJ/cm^2 and pulse number was 1000. For removing laser induced defects, we immersed black silicon in a solution (2 wt. % NaOH, 2 wt. % Na_2SiO_3, and 5 vol. % isopropyl alcohol) with temperature of 75–85 °C for different time. For solar cell fabrication, the n$^+$ emitter was formed with a liquid $POCl_3$ diffusion on front surface. Then, phosphor silicon glass (PSG) was removed with a buffered oxide etch (BOE) solution, Ti/Ag (500/1000 nm) was deposited by E-beam evaporation through a metal mask to form

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front grids. Finally, a 80 nm-thick SiN_x passivation layer was deposited by plasma enhanced chemical vapor deposition (PECVD). Several PT wafers were also added to solar cell fabrication for comparison as reference cells. Surface morphologies were characterized by a scanning electron microscope (SEM). Reflectance spectra were measured by a fiber spectrometer equipped with integrating sphere. Effective carrier lifetime was tested using a lifetime tester. Solar cell performance was obtained under a standard 1-sun illumination with a solar simulator and a sourcemeter. External/internal quantum efficiencies (EQE/IQE) of the cells were measured by a quantum efficiency tester. Each data obtained was based on an average of about 10 wafers/cells.

Figure 1 shows SEM images of typical untreated FS-BS surface and its evolutions upon different etching time. The conical spike structures are formed by a combination of laser ablation and melting in a SF_6 reactive gas ambient, as reported previously.[10,19] As shown in Fig. 1(a), spikes produced under energy of 1.82 kJ/cm^2 have a cross section diameter of 6–7 μm near the base tapering down to a sharp tip, with an average height of 10–15 μm. Plenty of laser re-deposited particles in bright color can be observed, whose thickness are typically 100–200 nm.

To remove laser induced defects, we performed a systematical wet etching on black silicon with prolonged etching time and then investigated their morphology evolution. In Fig. 1(b), after 3 min etching, the conical shape of spikes becomes blunt. Besides, we can also see many holes between these spikes, which are neglected in previous study. As shown in Fig. 1(c), after 5 min etching, the laser re-deposited particles covered on the spikes disappear and then the single crystalline core appears. The cross section of spikes turns into square in shape under anisotropic etching character of alkaline solution. When etching time extends to 7–9 min (Figs. 1(d) and 1(e)), spikes turn into upright pyramids and the holes become inverted pyramids, our work offers a way for forming such kind of morphology in addition to that of Kim *et al.*[20] As etching time is prolonged to 11 min (Fig. 1(f)), the MT surface is further polished. No further etching is made because laser induced defects are mostly removed after 11 min etching, which will be discussed in the following part.

To prove whether the surface recombination has been well suppressed by the etching process, we measured minority carrier lifetime values on modified FS-BS surface. Figures 2(a)–2(f) show lifetime mappings of the surfaces under the etching time from 0 min to 11 min, respectively. The inner square with brown color in Fig. 2(a) is untreated FS-BS region (11 × 11 mm^2), which has an average lifetime of 1.6 μs. Comparing to the bulk silicon lifetime, the lower lifetime value inside untreated FS-BS area indicates a higher surface recombination rate. For the cases of etching time of 3 min, 5 min, 7 min, 9 min, and 11 min (see Figs. 2(b)–2(f)), the average lifetime values inside modified FS-BS area are 2.3 μs, 4.1 μs, 15.9 μs, 18.0 μs, and 20 μs, respectively, which show a gradually lowered recombination center density. Lifetime inside modified FS-BS area in the case of 11 min is close to the bulk value, which indicates that most of the laser-induced defects have been removed. The suppressed surface recombination can reduce dark saturation current density (J_0) of solar cells.[14] For silicon solar cells, V_{oc} can be written as[21]

$$V_{oc} = \frac{kT}{q} \ln\left(\frac{J_{sc}}{J_0} + 1\right), \tag{1}$$

where k is Boltzmann's constant, T is temperature, q is the charge of an electron, and J_{sc} is the short circuit current. From Eq. (1), we can see that the reduction of J_0 can improve V_{oc} performances of the cells, which agrees well with our experimental results.

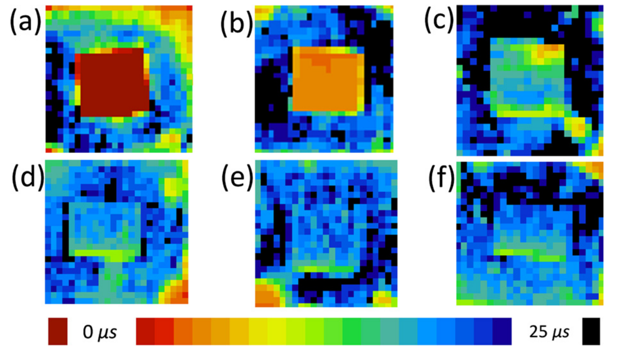

FIG. 2. Minority carrier lifetime evolution of modified black silicon surface as the etching time increasing from 3 to 11 min.

To evaluate light trapping ability of modified FS-BS surface after the etching, we measured surface reflectance as a

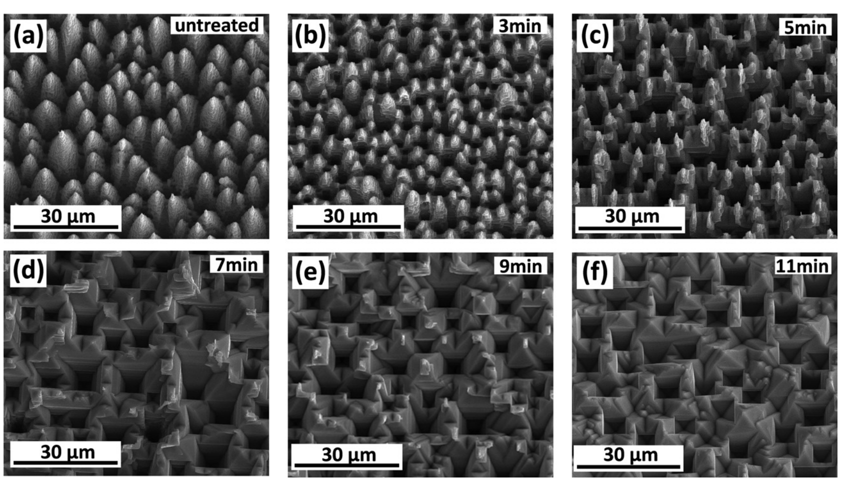

FIG. 1. SEM images of modified black silicon surface etched in an alkaline-based solution from 3 to 11 min.

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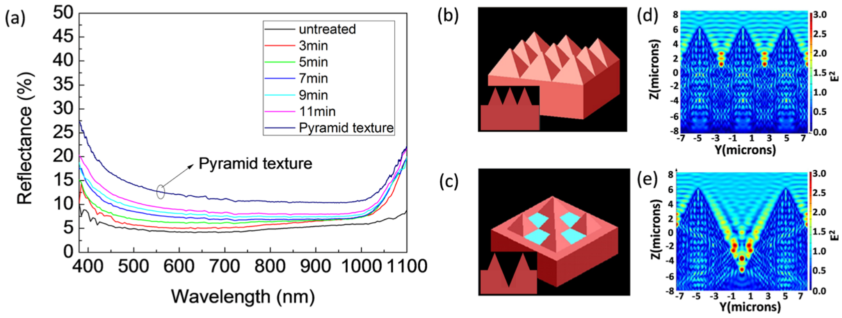

FIG. 3. (a) Reflectance spectra of modified black silicon surface under different etching time, and the PT surface is also used for comparison; (b) and (c) Schematic of PT and MT structures; (d) and (e) FDTD simulation of PT and MT structures.

function of etching time. Figure 3(a) shows the reflectance spectra of the result morphologies under the etching time from 3 min to 11 min, respectively. The reflectance of untreated FS-BS is around 5% in 400–1000 nm range, and then the value increases gradually as the increase of etching time, reaches ∼7%–12% under 3–11 min etching. Reflectance of typical PT is between 12%–15%, which is higher than FS-BS under all etching conditions. That means the MT morphology obtained by 11min etching of FS-BS shows advantageous for photon capturing than that of PT even after etching. Based on the results provided by Kim *et al.*[20] and Fan *et al.*,[22] the reflectance of MT is also lower than the surface with random distributed inverted pyramids[20] and close to optimized aligned inverted pyramid[22] surface based on lithography.

In order to further prove the advantages of MT morphology for photon harvesting as compared to that of conventional PT, we use finite difference time domain (FDTD) method to simulate the light intensity distribution for the two types of light trapping structures, as presented in Figs. 3(b) and 3(c). The upright and inverted pyramids are both set to 5 μm in width and 6 μm in height, which are close to the real cases as show in Fig. 1(f). The wavelength of light is chosen as 300–1200 nm. Figs. 3(d) and 3(e) are the corresponding simulation results. We can see clearly that a stronger electromagnetic field (EM) appears at the bottom of MT than that in the valleys between pyramids in PT, which shows enhanced photon capturing ability with a MT morphology is induced by a prolonged light path length and multiple reflections.

J-V and quantum efficiency characteristics of cells with modified FS-BS surface under different etching time are also tested to verify the effectiveness of defect removing on actual cell performance, as shown in Fig. 4. Untreated cell has a low V_{oc} of 303 mV, which is strongly related to the high recombination rate on untreated FS-BS surface and consistent with its low lifetime of 1.6 μs in Fig. 2(a), leading to a low CE of 2.2%. When the etching time increases from 5 min to 11 min with an interval of 2 min, the cells have a gradually increased V_{oc} of 463 mV, 527 mV, 544 mV, and 557 mV, respectively. The obtained average efficiency for 4 groups cells are 8.8%, 10.3%, 11.1%, and 12.3%, respectively. We have known that decreased surface recombination is benefit for the increase of V_{oc}, therefore, the CE of the cells has been evidently improved. While the variation of J_{sc} (shown in Fig. 4(a)) and EQE (shown in Fig. 4(b)) for all treated cells is small, we can analyze from two aspects: As the etching time increases, in one aspect, the increased carrier life time of the substrate (shown in Fig. 2) leads to a longer diffusion length of photon generated carriers,[21] so more carriers can be collected by the electrodes of the cell, as a result, J_{sc} increases; in another aspect, the etching also increases surface reflectance of the substrate (shown in Fig. 3(a)), which leads to less photons can be absorbed by the cell, as a result, the number of photon generated carriers decreases, so J_{sc} decreases. With the combination of the two effects, J_{sc} of all treated cells changes little. Form the IQE graph (shown in Fig. 4(c)), we can see clearly that the recombination rate on untreated FS-BS cell surface is so high, which prevents photon generated carriers to be collected in the entire 400–1100 nm range. Refinement of IQE in 400–600 nm range reconfirms that the improved CE is a result of suppressed surface recombination because short wavelength photons are only absorbed in the near surface of the substrate.

Finally, to prove the advantages of the reformed cells with modified FS-BS surface, comparisons are made among MT (11 min etching of FS-BS surface) cells, PT reference cells (fabricated at the same time with MT cells), and the optimized cell with femtosecond-laser treated surface in Nayak's work.[18] Aluminum back-surface-field (BSF) is added to MT cells and PT reference cells to make them with the same structure as Nayak's cell. The test results are shown in Table I. As compared to Nayak's cell, the MT cell in our work shows lower J_{sc} but higher V_{oc} and CE, which indicates the improved V_{oc} can greatly compensate the J_{sc} loss induced by reflectance degeneration, finally results in the promotion of CE. While as compared with the PT reference cells, the higher J_{sc} of MT cell in our work is caused by an enhanced photon capturing property of MT as discussed in Fig. 3, which eventually leads to a higher CE. However, the V_{oc} of MT cells is a bit lower than that of PT reference cells, and the CE advantage is not big, we think this is probably due to

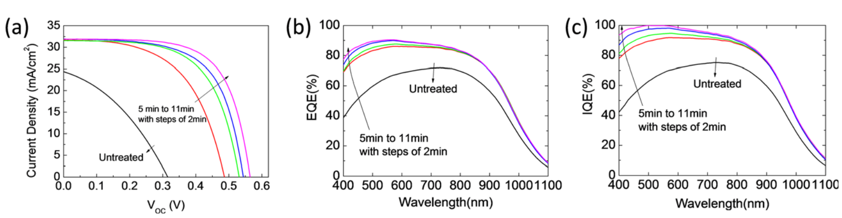

FIG. 4. Performance of solar cells based on modified black silicon surface: (a) J-V curves; (b) EQE; (c) IQE.

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TABLE I. Solar cell efficiency and J-V parameters of MT cell, PT cell, and Nayak's cell.

Samples	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	CE (%)
MT cell	590	36.0	73.6	15.6
PT cell	599	34.2	74.8	15.3
Nayak's cell[a]	507	39.2	71.4	14.2

[a]Results come from Ref. 18.

that there may be still some laser induced defects deep inside the spikes, which cannot be completely removed during the etching process.

In summary, we obtain a MT morphology by anisotropic-etching of FS-BS surface. The MT morphology has an advantage of light trapping ability over PT, leading to a higher J_{sc} in solar cell performance. Furthermore, the wet etching process can make the surface recombination inside modified FS-BS area be suppressed effectively, which leads to the evident increase of V_{oc}. Eventually, the solar cells based on modified FS-BS surface obtain an improved CE of 15.6%, which is higher than 15.3% of the PT reference cells. The findings in this work can be utilized to fabricate high performance silicon solar cells, which can also be easily applied to mass-production.

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