Characterization of the nanosized porous structure of black Si solar cells fabricated via a screen printing process*

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Abstract: A silicon (Si) surface with a nanosized porous structure was formed via simple wet chemical etching catalyzed by gold (Au) nanoparticles on p-type Cz-Si (100). The average reflectivity from 300 to 1200 nm was less than 1.5%. Black Si solar cells were then fabricated using a conventional production process. The results reflected the output characteristics of the cells fabricated using different etching depths and emitter dopant profiles. Heavier dopants and shallower etching depths should be adopted to optimize the black Si solar cell output characteristics. The efficiency at the optimized etching time and dopant profile was 12.17%. However, surface passivation and electrode contact due to the nanosized porous surface structure are still obstacles to obtaining high conversion efficiency for the black Si solar cells.

Key words: black silicon; noble metal nanoparticles; catalysis; nanosized porous; solar cells
DOI: 10.1088/1674-4926/33/6/064007 **PACC:** 8630J; 7340L; 7865H

1. Introduction

The surface reflectance (R) of silicon (Si) solar cells should be reduced to obtain a high efficiency. To date, pyramid surface structures can be formed via NaOH etching, which is currently widely used in production. Recently, considerable effort has been dedicated to the preparation and characterization of black Si[1−3], which suppresses reflection over a wide spectral bandwidth. The preparation of black Si is based on a mixture of HF and H_2O_2 solutions and H_2O. However, the solution does not etch Si except in the presence of noble metal catalysts. For the chemical etching of Si using a noble metal catalyst and aqueous solutions of HF and H_2O_2, the mechanism is based on the following reaction:

$$Si + H_2O_2 + 6HF \rightarrow 2H_2O + H_2SiF_6 + H_2 \uparrow .$$

Previous metal-assisted etching utilized a two-step process with noble metal nanoparticles either predeposited as nanoislands in evaporated thin metal layers[4,5] or predeposited via electroless plating[6,7]. However, these methods cannot control the metal size at a single nanosize over a large area. Another method involves predeposition using a nanoparticle colloid[8]. However, the stability of colloids is a major obstacle because colloids tend to aggregate or precipitate in solution. Considerable effort has been dedicated to this problem, and several methods have been developed[9−13]. In 2009, Yuan *et al.*[14] fabricated black Si solar cells with an efficiency of 16.8%, passivated with thermal SiO_2 and without an antireflection coating (ARC). They formed a Ti/Pd/Ag/Pd front grid via photolithography and deposition methods. The short-circuit current J_{sc} improved by 38%. This technique is expected to be applied to the fabrication of Si solar cells.

In the current study, black Si solar cells were fabricated using a conventional production method in the assembly line. We studied the relationship between the conversion efficiency of solar cells and the emitter dopant amount (sheet resistance) in black Si fabricated via chemical etching catalyzed by Au nanoparticles, which were deposited using a nanoparticle colloid.

2. Experimental

2.1. Black etching

Black Si was fabricated on a 180 μm (148.56 mm^2) p-Si (100) substrate with a resistivity of 1.5 Ω·cm. The process sequence started with saw damage removal via double-side polishing. Prior to etching, the Si wafer was dipped in a 0.4 mM/L[14] $HAuCl_4$ solution containing linear polyethylenimine (PEI, Mn is approximately 423)[11], which acted as both a stabilizer and a reducing agent, for 2 min at room temperature to prepare nanoscale metal particles. The initial molar ratio was 4 : 1 PEI : $HAuCl_4$[13]. Black etching was then performed by immersing the Si wafers in a mixture of HF, H_2O_2, and H_2O at a volume ratio of 1 : 5 : 10[5,15,16] at room temperature for 6 min.

* Project supported by the Knowledge Innovation Program of the Chinese Academy of Sciences (No. KGCX2-YW-382) and the National Program on Key Basic Research Project of China (No. 2010CB933804).
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Received 12 November 2011, revised manuscript received 27 December 2011

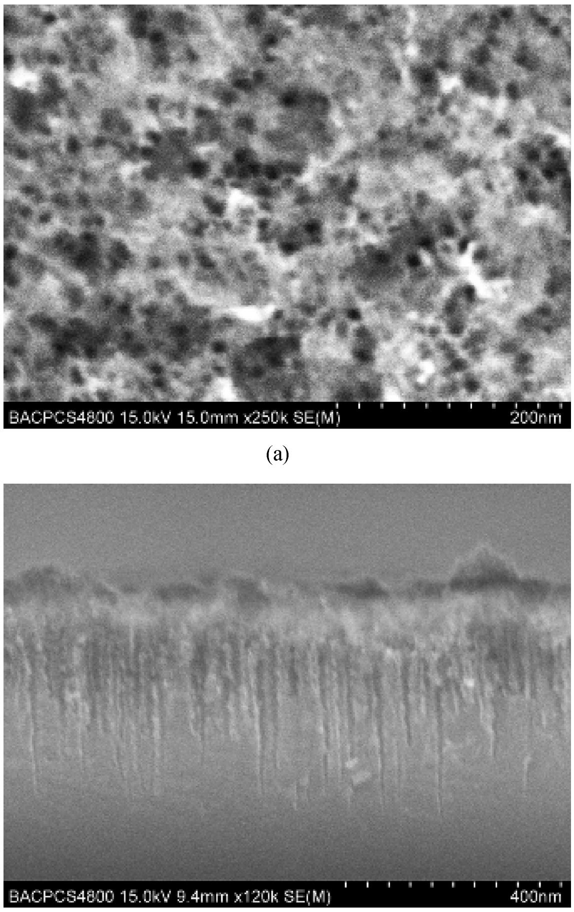

Fig. 1. SEM images of the sample. (a) Surface image. (b) Cross-section image.

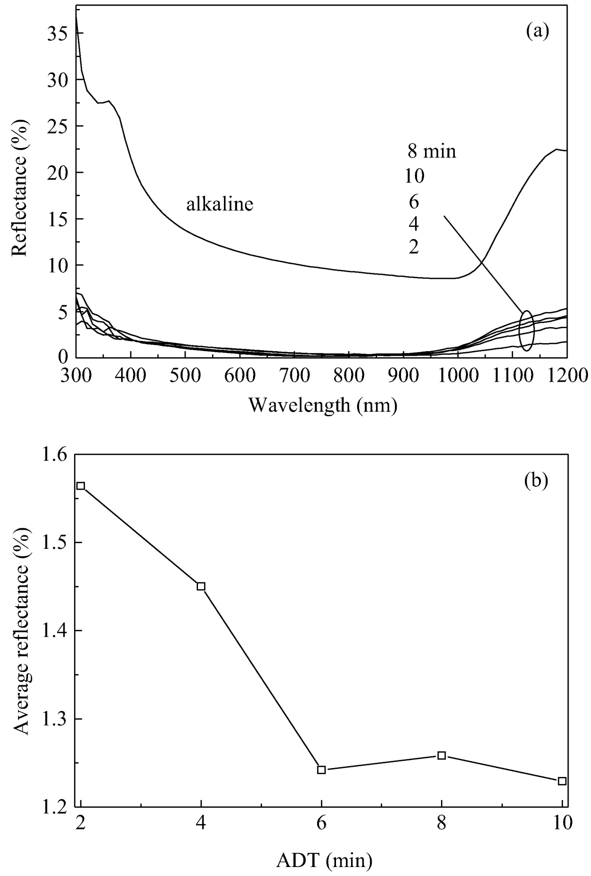

Fig. 2. (a) Reflectivity of the sample surfaces at various ADT. (b) ADT-dependence on the average reflectivity in the 300–1200 nm range.

2.2. Cell fabrication

Given that Au acts as a deep trap for carriers in Si, Au particles were removed in a $I_2 : NH_4I : H_2O = 1 : 4 : 40$ solution for 5 min at 80 ℃[17]. Au is a detrimental impurity in Si; thus, all black Si wafers were immersed in chloroazotic acid at 80 ℃ for approximately 20 min to further reduce the number of Au particles. A standard SCII cleaning solution ($HCl : H_2O_2 : H_2O = 1 : 1 : 6$) was subsequently applied to completely remove possible metal residues prior to black Si solar cell fabrication. The black Si solar cells were then fabricated using a Si solar cell manufacturing process. The n^+-emitter layer was formed via diffusion of $POCl_3$ for ~40 min at 840 ℃ (to produce 37 Ω/□ emitters) and 835 ℃ (to produce 46 Ω/□ emitters). A SiN_x:H film (80 nm, $n = 2.05$) was deposited on the front side to passivate the black Si layer. A front Ag grid electrode and a rear Al back surface field were formed via a corresponding screen printing of commercial paste and a firing process.

3. Results and discussion

A scanning electron microscope (SEM) image shows that the surface structure of black Si is in random cones [Fig. 1(a)]. Figure 1(b) shows the cross-section of the black Si substrate, which is clearly a nanosized porous structure.

Table 1. Minority carrier lifetime for the different samples after diffusion.

Etching time	Sheet resistance (Ω/□)	τ (μs)		
6 min	46	15.05	14.94	15.27
		14.86	14.81	14.71
		14.65	14.92	15.10
	37	14.89	15.33	14.99
		15.08	14.90	14.53
		13.90	14.09	14.53
Reference	45	12.20	10.50	13.52
		10.77	11.39	10.63
		14.09	15.01	14.99

Figure 2(a) shows that the reflectivity of the porous structure is dramatically reduced within the entire 300–1200 nm range (AM 1.5G) compared with the reference sample, which was etched using NaOH. Figure 2(b) shows the Au deposition time (ADT)-dependence on the average reflectivity (R_{bSi}) in the 300–1200 nm range. R_{bSi} sharply decreases as the ADT is extended from 2 to 6 min. However, the maximum R_{bSi} is less than 1.5%, which is significantly lower than that of the reference surface prepared using an alkaline solution texture with an ARC of 5%.

The substrates were immersed in a solution of I_2/NH_4I to remove Au particles. After the emitter formation, the minority carrier lifetime (τ) was measured using a Semilab-2000 (Ta-

Table 2. Black Si solar cell characteristics.

Etching time	$R_{\square}$ ($\Omega/\square$)		V_{oc} (mV)	I_{sc} (A)	FF (%)	E_{ff} (%)
6 min	46	Best	569.7	4.37	52.2	8.39
		Average	568.3	3.91	44.6	6.50
	37	Best	574.7	4.14	61.4	9.43
		Average	579.8	4.07	49.5	7.55
Reference cell	45	Best	626.8	5.54	77.9	17.5
		Average	620	5.5	77	17.2

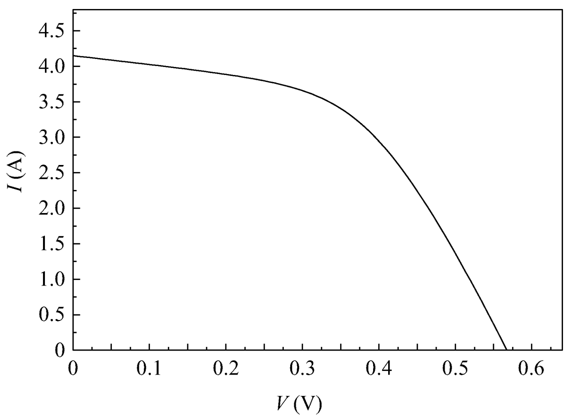

Fig. 3. I–V curve of the black Si solar cell.

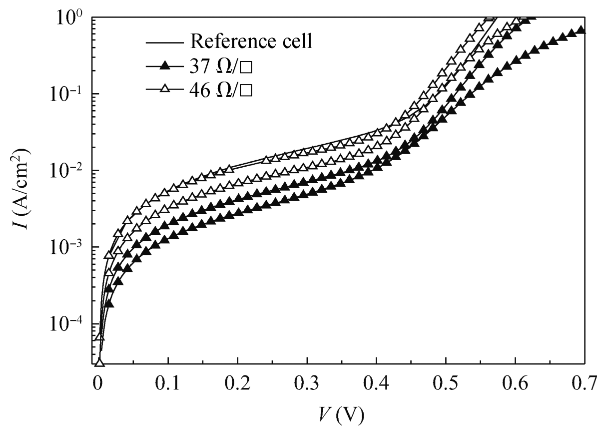

Fig. 4. Dark I–V test of all cells.

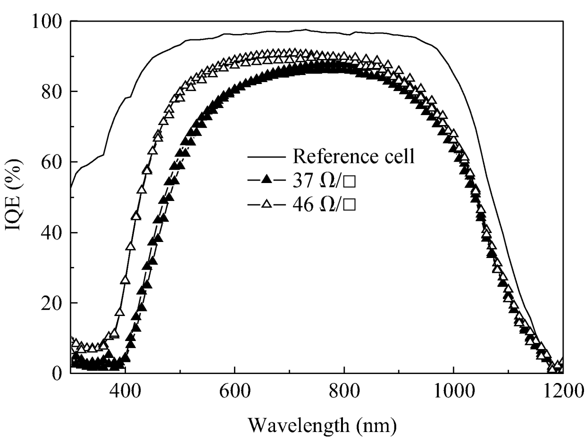

Fig. 5. IQE measurements of black Si solar cells.

ble 1). τ is higher than 10 μs, indicating that no Au contamination remained in the black Si emitter layer after Au particle removal.

The best output characteristics of the black Si cells are shown in Table 2. Compared with the reference cell, all the output parameters of the black Si solar cells are significantly lower, especially the fill factor (FF). From the I–V curve (Fig. 3), the serious resistance (R_s) and shunt resistance (R_{sh}) caused a decrease in the conversion efficiency. A large R_s not only lowers the short circuit current (I_{sc}), but also reduces the collection efficiency of the carriers. In addition, a sharp bend can be observed in the I–V curve line, which also leads to a decrease in FF. Normally, an ideal factor of the diode (n) higher than 2 ($n > 2$), led by the recombination of the depletion region, is the primary reason for such a bend. The open circuit voltage (V_{oc}) can be detrimentally affected if n is too large.

The data obtained from the light I–V characterization were used to compare the black Si solar cell performance of the 46 $\Omega/\square$ and 37 $\Omega/\square$ emitters. The differences are notable: in the latter case, the efficiency, V_{oc}, and FF are much higher, whereas R_s is much lower. These results indicate that a heavier dopant of the n^+-emitter is needed for black Si solar cells compared with conventional Si solar cells etched using NaOH.

Figure 4 shows that the dark current for both 46 $\Omega/\square$ and 37 $\Omega/\square$ samples shows a rapid increase at low voltages ($<$ 0.1 V), indicating that the shunt resistance (R_{sh}) of the cells is especially low. The R_{sh} of the 37 $\Omega/\square$ samples is much better than that of 46 $\Omega/\square$, although the dark current is still very high. From 0.2 to 0.6 V, the dark currents of all samples are significantly high. This result is attributed to a recombination of the depletion region, which is also the reason for the low V_{oc}. As a porous surface structure, the phosphorous diffusion emitter is not uniform. After the firing process, light dopant areas can be shorted by the Ag paste; this characteristic is also the reason for the poor R_s and R_{sh}.

The intrinsic quantum efficiency (IQE) of the black Si solar cells and the reference cell were also compared (Fig. 5). The IQE results reveal a significant reduction in the short wavelength of the black Si solar cells compared with the reference cell. From 400 to 900 nm, the IQE of black Si solar cells is even lower than 90%. However, the IQE of the 46 $\Omega/\square$ samples is much higher than that of the 37 $\Omega/\square$ sample, especially from 300 to 800 nm.

The IQE of the 37 $\Omega/\square$ emitter is much lower than that of the 46 $\Omega/\square$ sample in the 400 to 800 nm range because of the heavier dopant in the 37 $\Omega/\square$ emitter, which leads to a thicker dead layer that serves as an effective recombination center for the photocarriers. This characteristic is the reason for the lower I_{sc} and may lead to a worse blue response while improving R_{sh} and V_{oc}. The dead layer can degrade the spectral response of the solar cell, increase the recombination current

Table 3. Output characteristics of the optimized black Si solar cells.

Etching time	$R_\square$ (Ω/□)	τ (μs)			V_{oc} (mV)	I_{sc} (A)	FF (%)	E_{ff} (%)
4 min	46	16.97	16.52	B	619.0	4.66	60.9	11.33
				A	613.6	3.28	50.9	6.90
	31	12.29	12.17	B	617.6	4.73	64.5	12.17
				A	615.0	3.66	55.8	8.28

(n), and lower the V_{oc} of the cells. Compared with the reference cell, the IQE of the black Si cells is much lower within the entire 300–1200 nm range, even with the same sheet resistance (46 Ω/□). Therefore, the nanosized porous structure of the black Si exacerbates surface recombination. These results agree well with those of Yuan[18]. Therefore, surface passivation is highly important, yet it is also an obstacle at present.

As previously mentioned, the etching time for black Si should be reduced. In addition, the sheet resistance could be lowered. Reducing the etching time, it is difficult to obtain a uniform black surface on the large area substrates, however. And the surface reflectivity is higher which will result in a low J_{sc}. Accordingly, we reduced the etching time to 4 min and formed two groups, namely, 46 Ω/□ and 31 Ω/□.

The output parameters of the optimized black Si solar cells are significantly improved (Table 3; A: average, B: best cell), especially V_{oc}. The efficiency increased to 11.33% for the 46 Ω/□ sample when the etching time was shortened. Compared with the 46 Ω/□ emitter at 6 min etching, an increase of 2.94% (abs.) was obtained, and V_{oc} increased from 569.67 to 619 mV, which is close to the V_{oc} of the conventional cell (620 mV).

An efficiency of 12.17% was obtained when the fabrication processes were optimized through shortening the black Si etching time and lowering the sheet resistance. However, FF and I_{sc} are still very low because of the R_s and R_{sh}, which are affected by poor surface passivation.

4. Conclusions

A nanosized porous structure in random cones (black Si) is formed in an acid solution catalyzed by Au nanoparticles. An average reflectivity lower than 1.5% (AM 1.5G) in the 300–1200 nm range was obtained. Black Si solar cells were fabricated in the production line using a conventional Si solar cell production method. An efficiency of 12.17% was obtained by optimizing the black Si solar cell fabrication parameters. Although a nanoporous structure on a silicon surface can lead to a lower surface reflectivity, the increased superficial area of silicon surface acts as a dead layer and induces a higher surface recombination velocity. The deeper nanoporous hole is the most severe. Therefore, the following steps are proposed in designing black Si solar cells: (1) to reduce the surface recombination of the nanosized porous black Si layer, the etching time should be as short as possible to obtain a shallower etching depth; and (2) the sheet resistance should be low to reduce R_s and improve FF. The low sheet resistance is also favorable for R_{sh}. However, surface passivation and electrode contact properties still remain as major obstacles; both are due to the nanosized porous structure of the black Si surface.

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