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Influence of the texturing structure on the properties of black silicon solar cell

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ABSTRACT

An optimized textured structure is a key for high efficiency multi-crystalline silicon solar cell. In this work, black silicon wafers with various structures have been successfully produced by plasma immersion ion implantation. The surface morphology, reflectance and internal quantum efficiency have been investigated by atomic force microscope, spectrophotometer and quantum efficiency measurement system, respectively. Results show that nanohillocks with average height of 150–600 nm have been generated on black silicon surfaces by different texturing conditions, and the reflectance over the wavelength from 300 nm to 1100 nm decreases with increasing the height of nanohillocks, whereas the internal quantum efficiency worsens. The solar cell based on the optimized nanohillocks height of 300 nm yeilds efficiency of 15.99% with short circuit current of 34.0 mA/cm^2.

1. Introduction

As it is known, there can be as high as 40% reflectance on the surface of damage removed silicon due to abrupt change of refractive index on the interface between silicon and air [1]. Reducing surface reflectance to enhance light absorption is very important to improve the conversion efficiency of crystalline silicon solar cell. Generally, depositing anti-reflection coating (ARC) with intermediate refractive index (for example, SiN_x [2]) is very effective to reduce surface reflectance. However, surface texturing is a more permanent and effective solution to decrease reflections. Anisotropic etching of monocrystalline silicon in alkaline solution is effective to reduce surface reflectance and widely used in industry [3]. But it doesn't work well for multi-crystalline silicon (mc-Si) wafer due to randomly orientated crystallites. Instead, isotropic etching in acid solution is widely used in industry [4]. The reflectance of acid etched mc-Si is still as high as 25%, leading to a big light reflectance loss.

To further reduce surface reflectance of mc-Si solar cell, various texturing methods have been tried and investigated. One of the most promising methods to reduce reflection is producing nanostructured surface which is often termed as "black silicon" [5]. Torres et al. have produced black silicon by femtosecond laser and demonstrated that the electrical performances were improved compared to the solar cell with non-textured surface [6]. The black multi-crystalline silicon can also be fabricated by local metal-catalyzed wet-chemical etching, and the efficiencies of the black cells can be estimated to be in the 12–14% range [7]. Reactive ion etching (RIE) is widely used to form black silicon [5,8,9]. Zaidi et al. [10] have demonstrated that the RIE textured solar cell by applying additional ion damage removal treatments can show a better short circuit current density in comparison with the solar cell by wet-chemical textured surface. And Lee showed that the conversion efficiency of multi-crystalline silicon solar cell produced by damage-free reactive ion etching can reach as high as 16.32% [11]. In our previous work [12], the black silicon has been successfully produced by plasma immersion ion implantation (PIII). The microstructure and reflectance of the black silicon have been investigated.

In the present study, the black multi-crystalline silicon has been fabricated using plasma immersion ion implantation (PIII). The influence of texturing structure on the performance of black silicon solar cell will be studied in detail.

2. Experimental

In this work, p-type multi-crystalline silicon wafers obtained from the same ingot with thickness of 200 ± 20 μm, area of 156 mm × 156 mm, and resistivity of 1–3 Ω cm were employed. First, the damage on the surface induced by wire-cutting was removed by etching in 10% NaOH solution at 80 °C. After that, the black silicon wafers fabricated by plasma immersion ion implantation process with different conditions as shown in Table 1. Then all the black silicon wafers were subjected to acid washing in 2% HCl and followed in 10% HF to remove the contamination and

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oxides. The wafers were phosphorus doped using phosphorous oxychloride ($POCl_3$) as the dopant source at the temperature of 825 °C. Afterward all the wafers were subjected to edge etching and the removal of phosphosilicate glass (PSG) layer with diluted HF (10% by volume). Silicon-nitride layer with thickness of 80 nm and refractive index of 2.05 was grown by plasma enhanced chemical vapor deposition (PECVD) process. Finally, the front and back metallization of all the wafers were carried out by screen-printing technique and followed by baking and co-firing in a conveyer belt furnace. The fabrication process of acid textured solar cell was identical with that of black silicon solar cells.

Table 1
Conditions of fabricating black silicon wafers.

Conditions	The ratio of SF_6 to O_2	Voltage pulses (V)	Etching time (min)	Radio frequency power (w)
C1	2.5/1	−500	5	900
C2	3/1	−500	3	900
C3	3/1	−500	5	900
C4	3/1	−1000	5	900
C5	3/1	−1500	5	900

The microstructures as well as surface areas of the black silicon wafers were investigated by atomic force microscope (AFM). The surface reflectance was examined by a UV–VIS–NIR spectrophotometer (Varian Cary 5000) equipped with an integrating sphere detector in the wavelength from 300 nm to1100 nm. The sheet resistance was studied by Four-probe sheet resistance measurement with mapping mode. Internal quantum efficiency (IQE) was measured on a Solar Cell Scan 100 quantum efficiency measurement system. The performance of the solar cells was determined by the JR-1250 Solar Cell I. V. Tester and Sorter under one sun global solar spectrum of Air Mass (AM) 1.5 at 25 °C. The cross-sectional micrographs of Ag–Si contact of the solar cells were investigated with a JEOL JSM-7001 F field emission scanning electron microscope (FESEM).

3. Results and discussion

The photographs of the polished wafer and textured wafers (C1, C3, C5) are exhibited in Fig. 1. It can be demonstrated that we have successfully produced the black silicon wafers with homogeneous surfaces, and the wafers become more and more black varying with the texturing conditions from C1 to C5. The

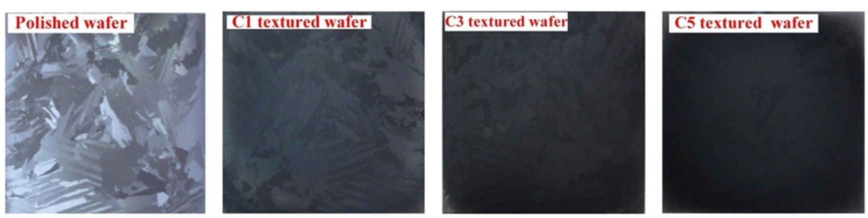

Fig. 1. Photographs of the polished silicon wafer and the black silicon wafers with the texturing conditions of C1, C3 and C5.

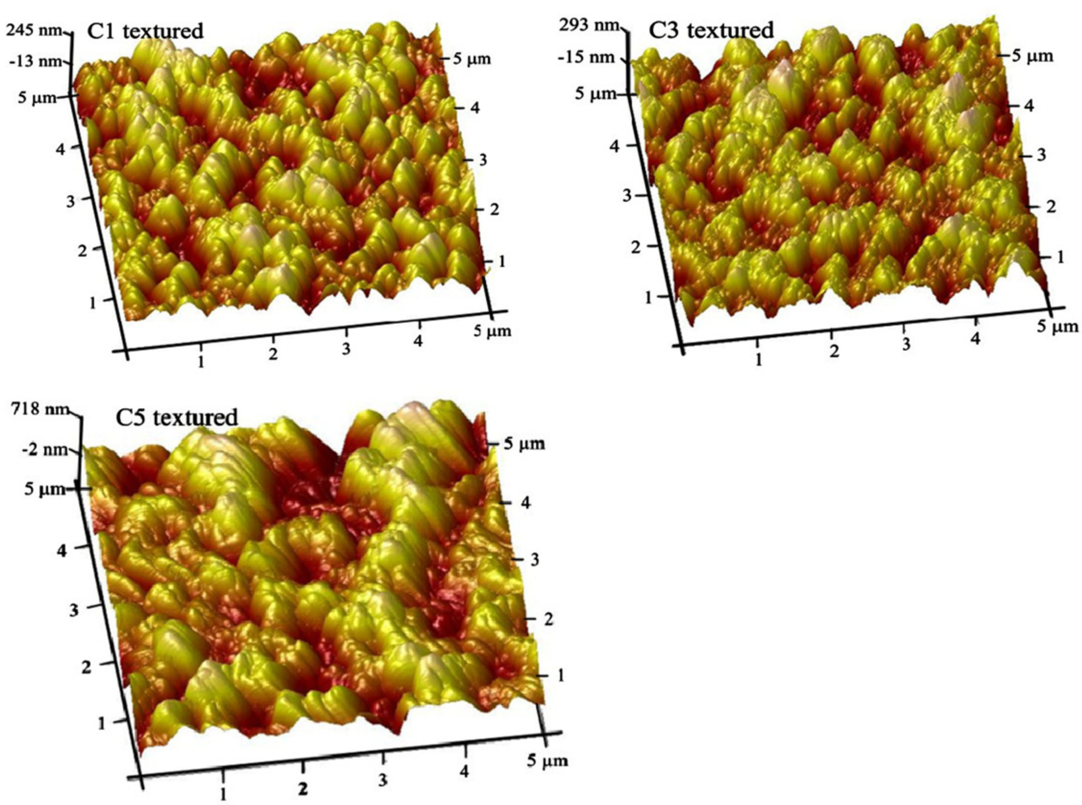

Fig. 2. AFM of the microstructures of the black silicon wafers with different texturing conditions. It typically shows that the black silicon surfaces are covered with dense nanohillocks, and the heights of the nanohillocks are 150 nm, 300 nm and 600 nm for the surfaces of the C1 textured, C3 textured and C5 textured, respectively.

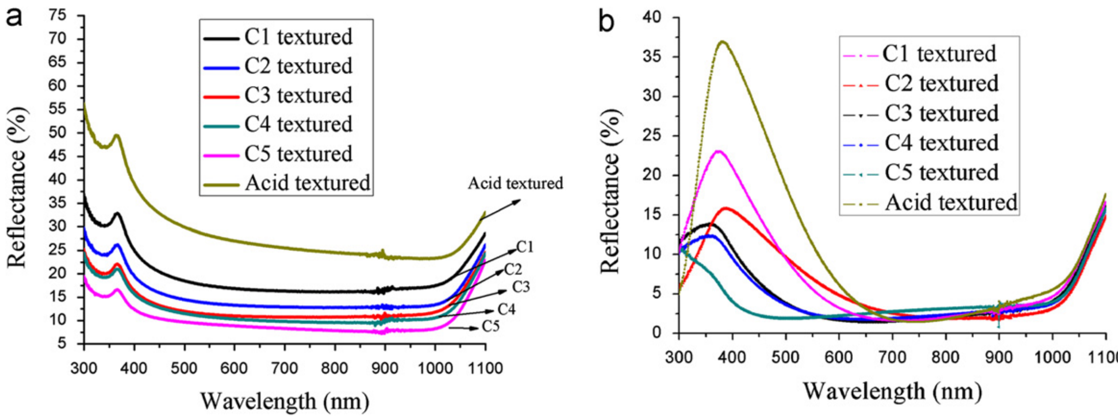

Fig. 3. (a) The reflectance of the wafers textured by different conditions. (b) The reflectance of the wafers coated with SiN_x layer.

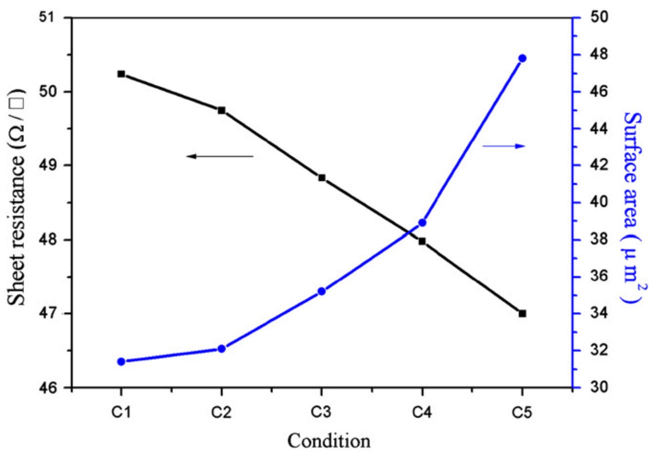

Fig. 4. The sheet resistance and surface area of the wafers textured by different conditions.

microstructures of the black silicons have been studied by atomic force microscope (AFM). The surface of the black silicon wafer is coverd with dense and random nanohillocks with the height of 150 nm, 220 nm, 300 nm, 450 nm and 600 nm for C1, C2, C3, C4 and C5 textured, respectively. Moreover, the lateral size of the C5 textured nanohillocks is enlarged compared to that of C1 textured nanohillocks. Fig. 2 typically shows the micrographs of the black silicon surfaces with texturing conditions of C1, C3, and C5. The microstructures of the black silicon wafers are the result of the competition between SF_x^+ ($x \leq 5$) and F^+ ions etching effect and $Si_xO_yF_z$ mask effect [12,13]. The competition between etching effect and mask effect is changed varying with the texturing conditions from C1 to C5, resulting in different microstructures.

Fig. 3(a) shows the reflectance of the black silicon wafers as-textured by C1, C2, C3, C4 and C5. The reflectance of acid textured wafer is also plotted for comparison. It can be seen that the reflectance of the black silicon wafers decreases varying with the texturing conditions from C1 to C5. However, the black silicon wafer textured by C1 still shows a strong decrease in the reflectance over the wavelength from 300 nm to 1000 nm compared to that of acid textured silicon wafer, which is the result of the unique microstructure of the black silicon. In general, the anti-reflection behavior of black silicon can be explained by effective medium approximation [1,14]. In the work, due to the lateral dimension of our black silicon approach 100 nm, the decreased reflectance should be explained by the combination effect of multiple reflections and diffraction. It is obvious that the nanohillocks structure is beneficial to increase the reflected times of the incident light between the surface structures. Moreover,

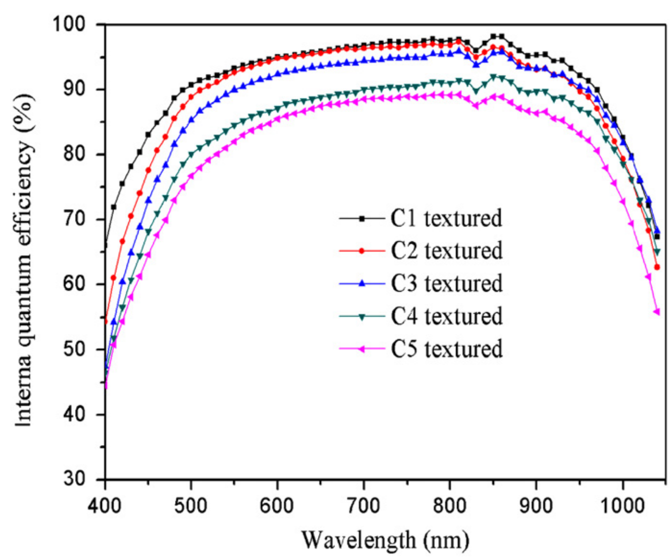

Fig. 5. The internal quantum efficiency of the solar cells textured by different conditions.

the diffraction effect is expected to occur when the dimension of the nanohillocks is comparable to the wavelength of the incident light, which makes the zero-order reflection weaken [15]. The decrease in the reflectance of the black silicon varying with the texturing conditions from C1 to C5 is attributed to that with increasing the height of the nanohillocks, the multiple reflections and diffraction effect become more obvious.

To understand the anti-reflection of the solar cells, the reflectance of the wafers coated with silicon-nitride was also measured, shown in Fig. 3(b). Obviously, after the deposition of SiNx layer, all the wafers textured by different conditions show a great decrease in reflectance, for instance, the reflectance of the wafer textured by C3 drops from 12.22% to 3.87% by application of the SiNx coating. Specially, in the range of wavelength from 600 nm to 1100 nm, they exhibit almost the same reflectance - approximately 2%. Therefore, we can conclude that the anti-reflection of the solar cells originates from nanostructure and SiN layer.

Fig. 4 exhibits the area of the textured surface (surface area) and the sheet resistance after diffusion. The surface area is extracted from AFM for an observation area of $5 \times 5\ \mu m^2$. With increasing the height of the nanohillocks, the surface area of the black silicon wafer increases, which contribute to easier P diffusion into the wafer, leading to a decreased sheet resistance. The internal quantum efficiency of the black silicon solar cells is presented in Fig. 5. It can be seen that the IQE over the short

Table 2
The performance of the black silicon solar cells with different texturing conditions. U_{oc} is open circuit voltage, J_{sc} is short circuit current density, R_{sh}, J_{rev} represent shunt resistance and shunt current density, respectively, FF means fill factor and E_{ff} means the photoelectric conversion efficiency of the solar cell.

Condition	U_{oc} (V)	J_{sc} (mA/cm^2)	R_{sh} (Ω)	J_{rev} (mA/cm^2)	FF (%)	E_{ff} (%)
C1	0.610	33.5	28	0.957	76.80	15.70
C2	0.615	33.9	27	0.888	75.71	15.78
C3	0.614	34.0	22	0.966	76.44	15.99
C4	0.605	33.2	16	1.529	77.07	15.49
C5	0.611	33.2	14	1.902	77.44	15.71

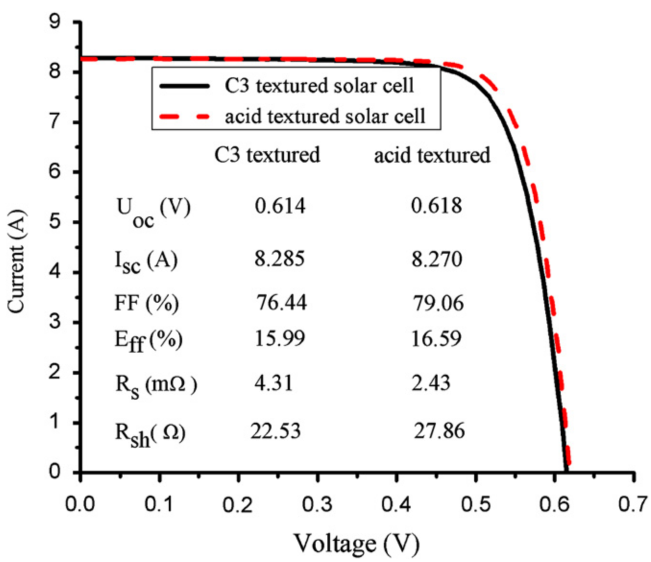

Fig. 6. Illuminated I–V characteristics of the C3 textured solar cell and acid textured solar cell.

wavelength worsens when changing the texturing conditions from C1 to C5. This can be attributed to the following: (i) the enlarged surface. Generally, the silicon surface has plenty of dangling bonds and traps that will play as effective recombination centers. The surface of black silicon enlarges varying with texturing conditions from C1 to C5. (ii) Increased Auger recombination. The sheet resistance declines with the increase of the height of nanohillocks, indicating that the doping concentration increases, while heavier doping concentration leads to higher Auger recombination [5]. (iii) Light scattering effect. The incident light can be scattered due to the nanostructure morphology, which will increase the interacting length of the incident light and silicon surface. Besides, increased damage to the surface plays a role in decreasing the IQE as well. In the long wavelength, the internal quantum efficiency also shows a decrease from C1 to C5, which is different from the result of F. Toor [16]. It may be attributed to the fabrication method of black silicon.

Table 2 lists the performance of the black silicon solar cell textured by C1, C2, C3, C4 and C5. Dramatically, the C3 textured solar cell, which has neither the lowest reflectance nor the best internal quantum efficiency, obtains the highest short circuit current density and conversion efficiency with the value of 34.0 mA/cm^2 and 15.99%, respectively. The optimal texturing condition is ascribed to the competition between reflectance reduction and IQE loss [5]. From Table 2, it can also be seen that the shunt current density increases and the shunt resistance decreases varying with the texturing conditions from C1 to C5. This originates from the enlarged surface and higher doping concentration, which cause larger surface recombination. It may also result from the increased uneven p–n junction with increasing the height of the nanostructure. From Fig. 6, it can be seen that there are little differences of short circuit current and open circuit voltage between C3 textured black silicon solar cell and acid textured silicon solar cell. However, the photoelectric conversion efficiency of the C3 textured solar cell is only 15.99% and that of acid textured solar cell is 16.59%, which is due to the difference of fill factor. As it is known, the fill factor is mainly

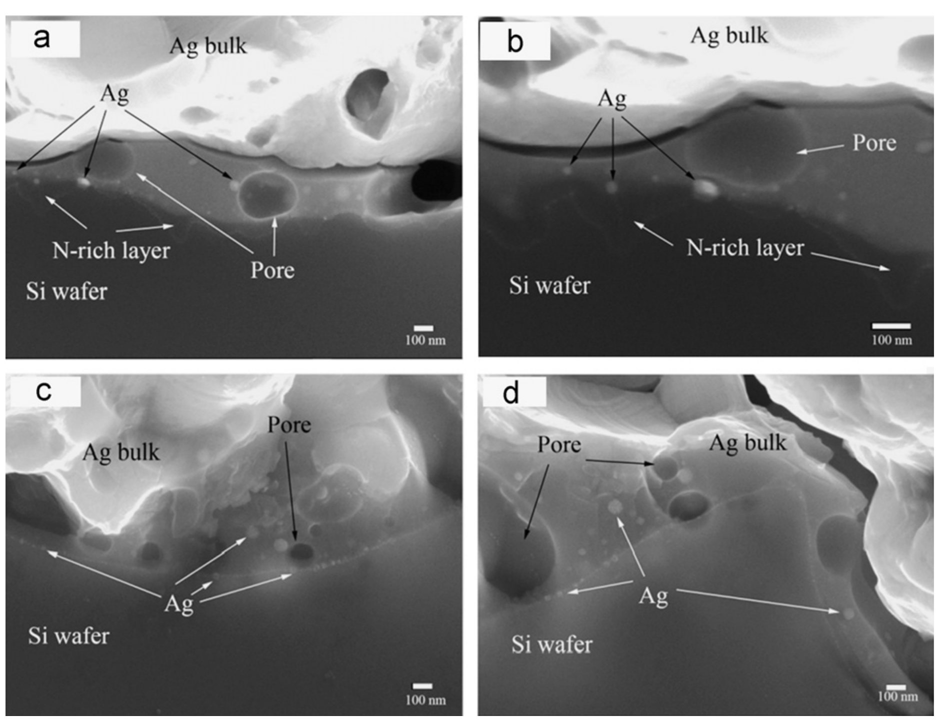

Fig. 7. Cross-sectional SEM micrographs of Ag–Si contact of the solar cells. (a) C3 textured, (b) C3 textured with bigger magnification, (c) the bottom of pit with acid textured, (d) the top of pit with acid textured.

affected by series resistance and shunt resistance. The series resistance of the C3 textured solar cell is almost twice than that of acid textured solar cell, resulting in inferior fill factor.

The reason for the higher series resistance can be illustrated by Fig. 7. It is known that the contact resistance between Si and Ag is an important component of series resistance. As it can be seen in Fig. 7(a) and (b) that there is N-rich layer remaining in the valley-bottom of the nanostructures of the black silicon surface, and Ag particles precipitated on the N-rich layer. The pores indicated in Fig. 7 are caused by gas which is generated by the reaction between Ag_2O and SiN_x [17]. It is believed that the current can be transported from the silicon into the Ag crystallites via a nearly ideal metal–semiconductor contact, which will result in low contact resistivity [18]. Therefore, the remaining N-rich layer between Si and Ag crystallites can lead to bad current transmission with high contact resistance. However, from Fig. 7(c) and (d), no remaining N-rich layer can be observed no matter in the bottom of pit or the top of pit textured by acid solution. A fine distribution of Ag crystallites is observed on the Si wafer, which results in low contact resistance.

4. Conclusion

The black multi-crystalline silicon has been successfully produced by plasma immersion ion implantation. The microstructures of black silicon exhibit different heights of nanohillocks with different texturing conditions. The reflectance and the sheet resistance of the black silicon decrease with increasing the height of nanohillocks. However, the internal quantum efficiency becomes worse due to increased surface recombination. The black silicon solar cell with the height of nanohillocks of 300 nm exhibits the highest conversion efficiency with the value of 15.99%. Its open circuit voltage and short circuit current are nearly the same with that of acid textured solar cell. However, its fill factor is much worse compared to that of acid textured solar cell, which originates from worse Ag–Si contact in the bottom of nanohillocks. The conversion efficiency of black silicon solar cell may be further improved by optimizing the surface passivation process and better Ag–Si contact.

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References

[1] L.L. Ma, Y.C. Zhou, N. Jiang, et al., Wide-band black silicon based on porous silicon, Applied Physics Letters 88 (2006) 171907.
[2] I.O. Parm, K. Kim, D.G. Lim, et al., High-density inductively coupled plasma chemical vapor deposition of silicon nitride for solar cell application, Solar Energy Materials and Solar Cells 74 (2002) 97–105.
[3] Z. Xi, D. Yang, W. Dan, et al., Investigation of texturization for monocrystalline silicon solar cells with different kinds of alkaline, Renewable Energy 29 (2004) 2101–2107.
[4] B. Gonzalez-Diaz, R. Guerrero-Lemus, B. Diaz-Herrera, et al., Optimization of roughness, reflectance and photoluminescence for acid textured mc-Si solar cells etched at different HF/HNO_3 concentration, Materials Science and Engineering B 159–160 (2009) 295–298.
[5] H.C. Yuan, V.E. Yost, M.R. Page, et al., Efficient black silicon solar cell with a density-graded nanoporous surface: optical properties, performance limitations, and design rules, Applied Physics Letters 95 (2009) 123501.
[6] R. Torres, V. Vervisch, M. Halbwax, et al., Femtosecond laser texturization for improvement of photovoltaic cells: black silicon, Journal of Optoelectronics and Advanced Materials 12 (2010) 621–625.
[7] S. Koynov, M.S. Brandt, M. Stutzmann, Black multi-crystalline silicon solar cells, Physica Status Solidi RRL: Rapid Research Letters 1 (2007) 53–55.
[8] J. Yoo, G. Yu, J. Yi, Black surface structures for crystalline silicon solar cells, Materials Science and Engineering, B 159–160 (2009) 333–337.
[9] W.A. Nostischka, O. Voigt, P. Manshanden, et al., Texturisation of multi-crystalline silicon solar cells by RIE and plasma etching, Solar Energy Materials and Solar Cells 80 (2003) 227–237.
[10] S. Zaidi, D. Ruby, J. Gee, Characterization of random reactive ion etched–textured silicon solar cells, IEEE Transactions on Electron Devices 48 (6) (2001) 1200–1206.
[11] K. Lee, M. Ha, J. Kim, et al., Damage-free reactive ion etch for high-efficiency large-area multi-crystalline silicon solar cells, Solar Energy Materials and Solar Cells 95 (2011) 66–68.
[12] Y. Xia, B. Liu, J. Liu, et al., A novel method to produce black silicon for solar cells, Solar Energy 85 (2011) 1574–1578.
[13] Y. Xia, B. Liu, S. Zhong, B. Chao, X-ray photoelectron spectroscopic studies of black silicon for solar cell, Journal of Electron Spectroscopy and Related Phenomena 184 (2012) 589–592.
[14] S. Koynov, M.S. Brandt, M. Stutzmann, Black nonreflecting silicon surfaces for solar cells, Applied Physics Letters 88 (2006) 203107.
[15] K. Hadobás, S. Kirsch, A. Carl, et al., Reflection properties of nanostructure-arrayed silicon surfaces, Nanotechnology 11 (2000) 161–164.
[16] F. Toor, H.M. Branz, M.R. Page, et al., Multi-scale surface texture to improve blue response of nanoporous black silicon solar cells, Applied Physics Letters 99 (2011) 103501.
[17] K.K. Hong, S.B. Cho, J.S. You, Mechanism for the formation of Ag crystallites in the Ag thick-film contacts of crystalline Si solar cells, Solar Energy Materials and Solar Cells 93 (2009) 898–904.
[18] G. Schubert, F. Huster, P. Fath, Physical understanding of printed thick-film front contacts of crystalline Si solar cells—review of existing models and recent developments, Solar Energy Materials and Solar Cells 90 (2006) 3399–3406.