A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
Volume 58 2013 Issue 1
DOI: 10.2478/v10172-012-0188-z

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SILICON SOLAR CELLS EFFICIENCY IMPROVEMENT BY THE WET CHEMICAL TEXTURIZATION IN THE HF/HNO_3/DILUENT SOLUTION

POPRAWA SPRAWNOŚCI KRZEMOWYCH OGNIW SŁONECZNYCH POPRZEZ CHEMICZNĄ TEKTURYZACJĘ W ROZTWORACH HF/HNO_3/ROZPUSZCZALNIK

The paper presents the results of the texturization process of the multicrystalline silicon wafers carried out in ternary HF/HNO_3/diluent solution, where the diluent was either CH_3COOH or H_2O, at varying HF/HNO_3 volume ratio and different time of texturization process. The technique of scanning electron microscopy was used to characterize the morphology of the obtained multicrystalline silicon surfaces, with subsequent surface reflectivity measurements. The appropriate selection of mixture components lead to a significant reduction in the reflectivity of the incident solar radiation in the relatively short time of 60 seconds. The resultant electric parameters were nearly the same as those for the commercial samples but obtained after 3 minutes.

Keywords: texturization, acid etching, multicrystalline silicon, silicon solar cells, photovoltaics

Autorzy zaprezentowali wyniki badań dotyczących procesu teksturyzacji w roztworze HF/HNO3/rozpuszczalnik stosowanego dla płytek krzemu multikrystalicznego, gdzie jako rozpuszczalnik stosowano zamiennie CH_3COOH oraz H_2O. W badaniach jako zmienne przyjęto objętościowy stosunek HF/HNO_3 oraz czas procesu. Morfologia powierzchni uzyskana po chemicznej modyfikacji krzemu została scharakteryzowana przy użyciu skaningowej mikroskopii elektronowej, a następnie zbadano wpływ takiego ukształtowania powierzchni na odbicie promieniowania słonecznego. Autorzy wykazali, że odpowiednie dobranie składu mieszaniny trawiącej pozwala na uzyskanie najniższych wartości odbicia w stosunkowo krótkim czasie 60 sekund. Ponadto parametry elektryczne zmodyfikowanych ogniw słonecznych nie odbiegały od tych uzyskanych komercyjnie w czasie trzykrotnie dłuższym.

1. Introduction

Continuous growth of the global annual energy consumption gives rise to an interest in photovoltaics devices. The current annual solar irradiation to the earth is much higher than energy demand and even plus established global energy resources [1]. At present, the production of solar cells has been dominated by the silicon devices and found to be about 75% of all the produced cells and multicrystalline silicon (mc-Si) solar cells account for around 50% of worldwide photovoltaic (PV) market [2, 3]. The multicrystalline silicon (mc-Si) is commonly used in PV industry because of its nontoxicity, abundance and the lowest manufacturing cost at the mass production level [4]. One of the many ways to improve both the conversion efficiency of silicon solar cells and to lower the production costs is to modify the silicon active surface due to the saw damage removal and creation of the surface texture which results in the reflectance decrease [5]. The surface texturization influences the light absorption in two ways. Firstly, the front surface is less reflective since each incident light hits the material at least twice. Secondly, the absorbed light path is longer because of multiple internal reflection from textured surface [6]. There are several methods which are suitable for proper surface texturing like laser methods [7, 8], the popular nowadays reactive ion etching (RIE) [9] and two new approaches of honeycomb-textured structures dry etching [10] and chemical treatment using metallic catalyst [11]. These techniques are promising but they required complicated installation and significant lowering of process time as well as costs of production is necessary.

Therefore, the acid etching is the most appropriate technique for the mass production level because of its one-step process, low cost and isotropic texturing which is not dependent on the crystallographic microstructure [4, 12, 13]. The commercially produced surface textures, using the HF/HNO_3 solutions, consist of the oval pits of several micrometers size (Fig. 1), however, inhomogeneously distributed.

The aim of this study was to find the appropriate composition of the texturing mixture in order to obtain the effective isotropic surface texture of the mc-Si solar cells and thus to improve the optoelectronic parameters.

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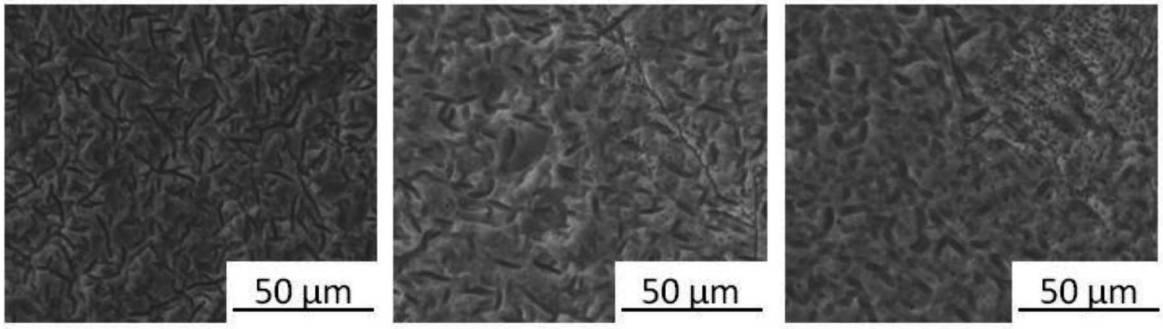

Fig. 1. Examples of commercially produced surface textures [14]

2. Experimental

Material used in the experiments was 'as cut', p-type, 0.5-3 Ωcm multicrystalline silicon wafers 'Swiss Wafers BG', of a square shape 25 cm^2 and 200 μm in thickness. The wafers were selected with respect to the same crystallographic orientation, fraction and arrangement of the grains. Before processing, the wafers were cleaned in acetone at elevated temperature. The texturization process was carried out in HF-HNO_3-diluent solution, where the diluent was either CH_3COOH or H_2O, at varying HF/HNO_3 volume ratio and different time of texturization process. In order to eliminate many variables, the content of diluents equal to 10% was kept constant.

Figure 2 presents the concentration triangle of HF-HNO_3-diluent. The open circles denote the literature data for the texturization of mc-Si wafers leading to a significant reduction in reflectivity and high values of the short circuit current [13] or appropriate surface texture [4]. These data were used to plan own experiment and the composition of the selected solutions (see black circles in Fig. 2). The surface morphology of the selected mc-Si wafers was studied using Scanning Electron Microscopy (SEM) Quanta 200 3D (FEI).

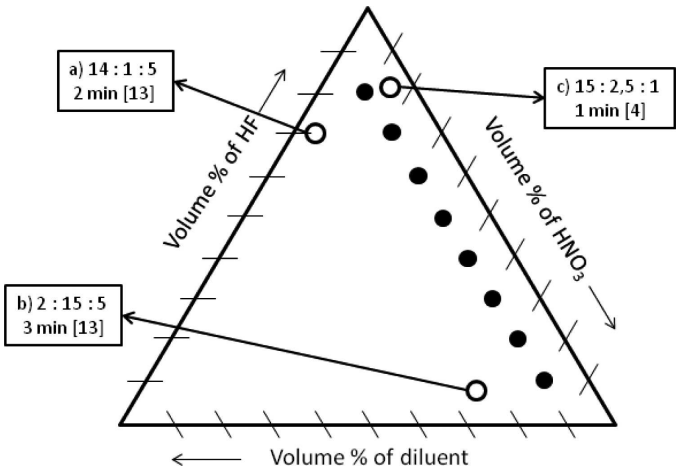

Fig. 2. Volume concentration triangle of HF-HNO_3-diluent. The compositions examined in the present experiment are indicated by black circles. Open circles denote the compositions described in the Ref. [4, 13]

For all the investigated samples (black circles in Fig. 2) several variables were selected. The HF/HNO_3 ratio was established between 8:1 and 1:8. The process time was in the range from 15 to 180 seconds. For comparison, a reference sample, with no surface texture, was also investigated. The only chemical treatment applied was saw damage removal in KOH:IPA:H_2O(DI) solution at 80°C for 3 min. An Ocean Optics QE 65000 spectrometer with integrated light source DH-2000-BALL was used to measure the surface reflectivity.

The following steps were involved in the production of mc-Si solar cells: p-n junction formation by diffusion from $POCl_3$ as a source at temperature 850°C for 25 min (20 min pre-diffusion and 5 min re-diffusion) resulting in the surface resistance R_s = 53 Ω/□; phosphorous silica glass PSG removal using 10% HF; passivation by the thermal oxidation at 800°C for 10 min; antireflective coating deposition of TiO_x by CVD method; screen-printing ohmic contacts using Ag and Al pastes (Du Pont PV 159, PV 381); firing in III-zone belt IR furnace.

The effect of surface morphology on the light current-voltage (LIV) characteristics was examined using simulator calibrated by the reference cell measured at the Institut für Solarenergieforshung GmbH Hameln/Emmental. The measurements were made at AM 1.5, light intensity of 1000 W/m^2 and temperature of 25°C.

3. Results

The acid texturization in the HF:HNO_3:diluent solution is a relatively short process in which it is possible to modify the silicon surface at room temperature. Undoubtedly, an advantage of this method is the simultaneous removal of the defected surface layer after diamond saw cutting and texturization in a one-step process. The first assessment of the silicon wafer surface was accomplished using unaided eye (Figs. 3a-e), while the closer look at the microstructure was performed by means of the scanning electron microscopy (Figs. 3f-j).

The SEM studies show directly that the surface after etching in solutions with HF/HNO_3 ratio between 0.5 and 2 is smooth (Fig. 3h). This is undesirable morphology because it acts as mirror reflecting the incoming solar radiation and thus, leading to large losses and to the decrease of the conversion efficiency. Therefore, the best seems to be wafer after texturing in a mixture of extreme component content that is at high HF (Fig. 3f) and high HNO_3 (Fig. 3j) amount. As the resulting microstructures were similar, further examination was focused on the solution of 8HF:1HNO_3:1H_2O.

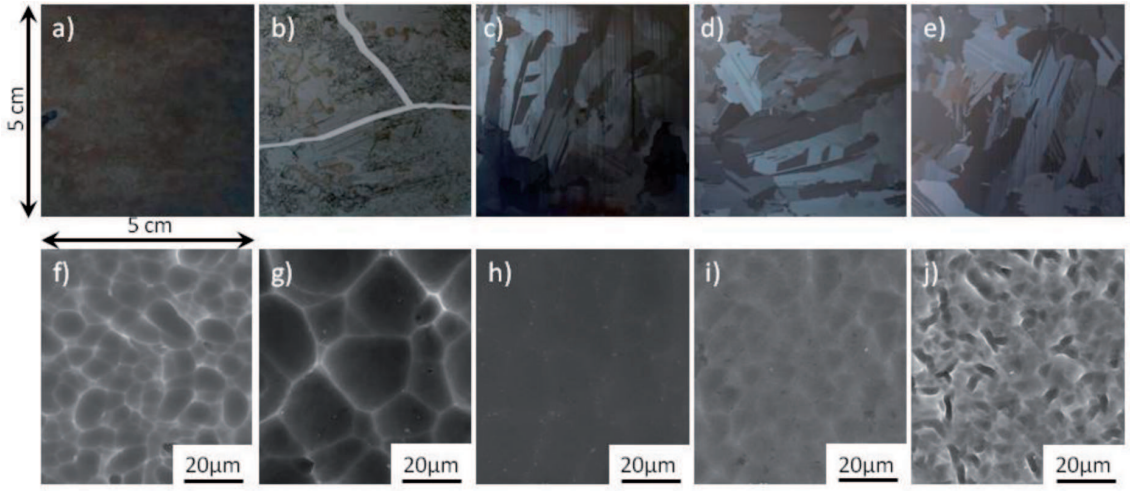

Fig. 3. Photos (a-e) and SEM images (f-j) of silicon surface after acid texturization in the HF/HNO_3 ratio of 8:1 (a, f), 7:2 (b, g), the range of 6:3 to 3:6 (c, h), 2:7 (d, i), 1:8 (e, j), for 60 seconds, with deionized water as a diluent

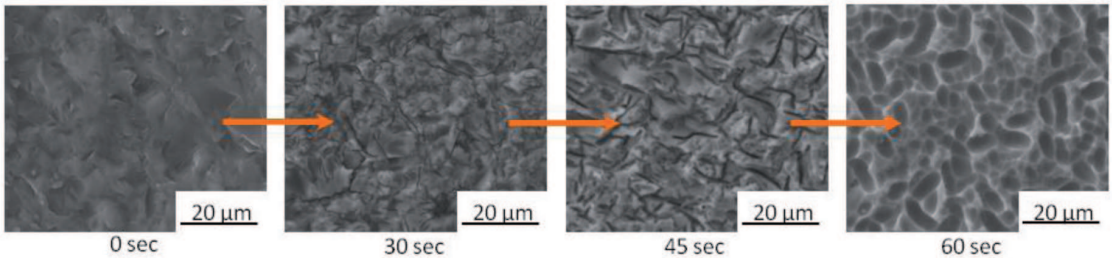

Fig. 4. SEM images of subsequent Si surface after texturing in the 8HF:1HNO_3:1H_2O mixture in relation to the process time

Figure 4 shows the subsequent images of the silicon wafer surface after various processing time. The microstructure shown in Fig. 4 after 45 seconds of etching is almost the same as that shown in Fig. 3j. This means that the silicon etching in the 8HF:1HNO_3:1H_2O solution is faster and leads to a satisfactory result in a shorter time. In addition, it was noted that in order to produce the proper surface texture the etching process has to be carried out longer, at least for 1 minute. Therefore, the examination of opto-electric parameters were performed only for the samples etched for time longer than 60 seconds.

In order to prove that described surface microstructure truly stops the incoming solar radiation, the material reflectance measurements were performed (Figs. 5 and 6) for two types of diluents (deionized water and acetic acid) and related to the reference sample (see black curves in Figs. 5 and 6). It is visible that the texturization in the solutions with deionized water as the diluent, leads to larger reduction in the reflectance (Fig. 6). Moreover, in both cases the best results were obtained for the solutions with HF as a dominant component and, surprisingly, for a relatively short time of 60 seconds.

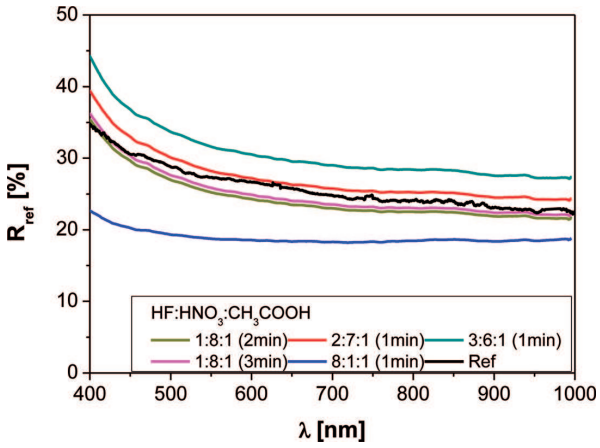

Fig. 5. Reflectivity of the mc-Si wafers versus the wavelength in the range of 400-1000 nm after texturization process in various conditions with CH_3COOH as a diluent

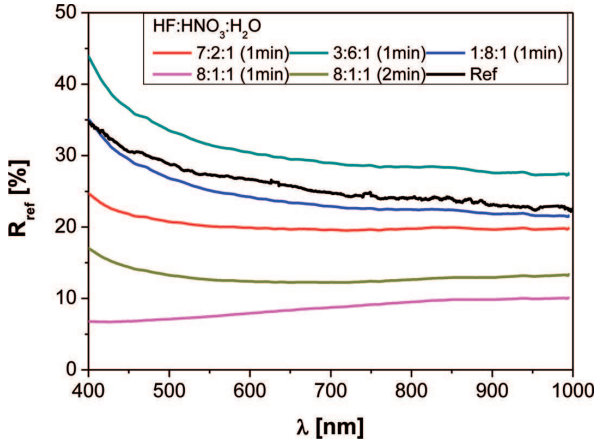

Fig. 6. Reflectivity the mc-Si wafers versus wavelength in the range of 400-1000 nm after texturization process in various conditions with H_2O as a diluent

The data collected in Fig. 5 and 6 allowed to calculate so-called effective reflectance(R_{eff}) in the wavelength range 400-1000 nm using Eq. (1) [15]:

$$R_{eff} = \frac{\int_{400}^{1000} R_{ref}(\lambda) N_{ph}(\lambda) d\lambda}{\int_{400}^{1000} N_{ph}(\lambda) d\lambda} \quad (1)$$

where: $N_{ph}(\lambda)$ – number of photons incident on a unit area for a given wavelength in one second for the solar spectrum AM1.5,

$R_{ref}(\lambda)$ – reflectance value referring to a particular wavelength.

The calculated R_{eff} values (Table 1) confirm the previous observation that the smooth Si surfaces resulted in the increase of the reflection from that surface (Table 1, samples No 4 and 7). In addition, the type of diluent was crucial. For CH_3COOH the reflectance reduction was at the level of 27.7% (sample No 5) while for the deionized water was even 67.3% (sample No 9). The sample No 6, which microstructure corresponds to that presented in Fig. 3j, shows the effective reflectance comparable to the reference sample (26.0%).

TABLE 1
R_{eff} values of mc-Si wafers after texturization process for various mixture content and processing time

No.	Type of diluent	$HF:HNO_3$: diluent	Time of texturization process [sec]	R_{eff} [%]
1	CH_3COOH	1:8:1	120	24.3
2		1:8:1	180	24.9
3		2:7:1	60	27.1
4		3:6:1	60	30.5
5		8:1:1	60	18.8
6	H_2O	1:8:1	60	24.2
7		3:6:1	60	30.4
8		7:2:1	60	20.1
9		8:1:1	60	8.5
10		8:1:1	120	12.8
Ref – sample with no surface texture				26.0

The most important for the users of photovoltaic devices are the electric properties of the solar cell. The current-voltage characteristics are shown in Fig. 7. For all presented samples after texturization process the short circuit current values are higher by at least 4% with respect to the reference sample with no texture. This reference cell is also characterized by a low fill factor of the I-V curve at the level of 66%. The application of the surface texture irrespective of the conditions, improved the fill factor of I-V curve to 75%. The short circuit current values are nearly the same while the highest open circuit voltage was obtained for the wafer textured in the $1HF:8HNO_3:1H_2O$ solution for 3 minutes as it was proposed by Kim et.al. [13]. However, similar result was obtained for the texturing in the $8HF:1HNO_3:1H_2O$ solution for 60 sec. This gives a three times reduction of the process time and thus a significant reduction in costs. It is also important to note that the texturization in $1HF:8HNO_3:1H_2O$ solution but for 60 seconds did not improve the open circuit voltage due to the insufficient surface development.

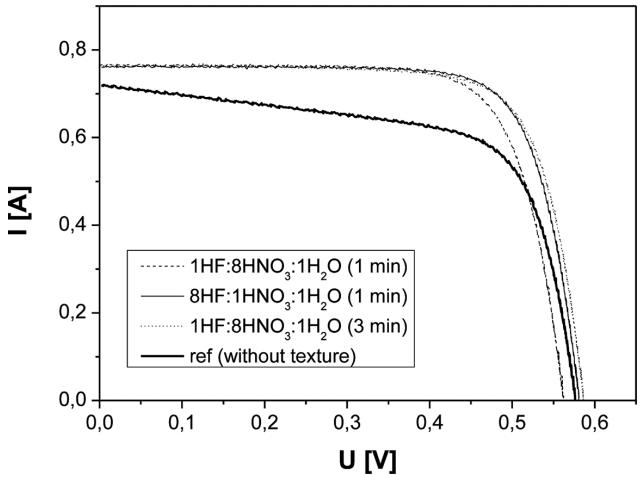

Fig. 7. Current-voltage characteristics of 25 cm^2 mc-Si solar cells depending on mixture content and time of texturization process

4. Conclusions

The acid texturization in the $HF:HNO_3$:diluent (CH_3COOH or H_2O) mixture of mc-Si wafers resulted in the saw damage removal and creation of the isotropic texture in the single step. The surface of mc-Si wafer textured in $8HF:1HNO_3:1H_2O$ solution shown favorable oval pits morphology. Therefore, it was possible to shorten the texturization process time to 60 seconds, that is three times less with respect to the results presented in the literature. Simultaneously, the solar cell possessed nearly the same high electrical parameters. The obtained results are attributed to a significant reduction of incoming solar radiation effective reflectance to the value of 8.5%, which means lowering by 67.3% relative to the sample without surface texture.

Acknowledgements

This research was support by European Union within European Social Fund realization under the project No. POKL.04.01.01-00-004/10 'Interdisciplinary PhD Studies in Materials Engineering with English as the language of instruction'. The SEM examination was performed in the Accredited Testing Laboratory of the Institute of Metallurgy and Materials Science of the Polish Academy of Sciences in Cracow.

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Received: 10 February 2012.