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Contribution of the photoluminescence effect of the stain etched porous silicon in improvement of screen printed silicon solar cell performance

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Abstract - *In this work, we investigate the potential use of porous silicon (PS) nanostructures stain etched into photovoltaic technology as one possible way to increase the silicon solar cell (SC) efficiency at low cost. The process is based on a combination of texturization and porous silicon formed by metal assisted etching which used the screen printed front grid contact. The photoluminescence (PL), the reflectivity spectra of the PS layers, spectral response and electrical measurements are presented and discussed. As a result, the short circuit current density was improved by more than 21%. We observed an increase in internal quantum efficiency (iQE) in the region where the PL of the PS layers appears and the minority carriers' diffusion length is enhanced by more than 60 µm. We report the correlation between the converter PL intensity and iQE and we demonstrate that the photoluminescence properties and the increased photocurrent result in an improvement of the solar cell efficiency.*

Résumé - *Dans ce travail, nous étudions la possibilité d'utiliser des nanostructures de silicium poreux (PS) gravé dans la technologie photovoltaïque comme un moyen possible d'augmenter l'efficacité de la cellule solaire au silicium (SC) à moindre coût. Le procédé est basé sur une combinaison de texturation et de silicium poreux formé par le métal en une gravure assistée qui utilise la grille de contact avant impression. La photoluminescence (PL), les spectres de réflectivité des couches PS, la réponse spectrale et les mesures électriques sont présentées et discutées. En conséquence, la densité de courant de court-circuit a été améliorée de plus de 21%. Nous avons observé une augmentation du rendement quantique interne (iQE) dans la région où la PL des couches PS apparaît et la longueur de diffusion des porteurs minoritaires est renforcée par plus de 60 µm. Nous rapportons la corrélation entre l'intensité du convertisseur PL et iQE et nous démontrons que les propriétés de photoluminescence et l'augmentation du résultat relatif au courant photoélectrique à une amélioration de l'efficacité des cellules solaires.*

Keywords: Silicon solar cell - Porous silicon – Photoluminescence.

1. INTRODUCTION

Porous silicon, 'PS' is a material creating great scientific and technological interest because of its ample range of applications [1-3]. Such material is very promising for application to silicon solar cells [4, 5], due to its combination of light trapping, antireflection properties and light conversion ability [6, 7].

The most used porous silicon layers, 'PSL' formation method has been the electrochemical method [8, 9]. However, the implementation of this technique in a

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production line of solar cells is quite difficult. The alternative PSL formation process by stain etching has been chosen to be applied in silicon-based solar cells. In a stain etching process, the silicon sample is simply immersed in a HF: H_2O_2: EtOH mixture and the PSL is obtained in a few seconds [10].

A very promising cost-saving alternative approach which avoids completely the deposition of metal nanoparticles and uses instead the screen-printed front Ag grid contact of monocrystalline silicon solar cells.

In this paper, we successfully apply this process to randomly textured monocrystalline silicon solar cells. In addition to improving the photovoltaic properties, other properties of porous silicon are taken advantage of in this study. It has been shown that, for a solar cell, there are two possibilities to use the high energy part of the solar spectrum (350-550 nm) more efficiently: photoluminescence and down-conversion [11].

The application of a luminescent down-shifting layer has been proposed as a method for improving the poor spectral response of solar cells in the short-wavelength range [12]. The layer absorbs photons, typically in the 300-500 nm spectral range, and reemits them at a longer wavelength where the photovoltaic device exhibits a higher response.

In this paper, we concentrate also on down-conversion and photoluminescence and assess the potential of the porous silicon layer formed by chemical treatment using the solar cell Ag front contact as catalyst. Our approach presents the advantage that the efficiency is improved by adding a component to a completed solar cell which can be optimized independently from the solar cell material itself.

2. EXPERIMENTAL DETAILS

Solar cells were fabricated using 4-inch solar grade Cz growth (100) – oriented silicon wafers, 450μm in thickness, p-type (boron doped) of 0.5-3 Ωcm resistivity.

Random pyramid surface texturization was carried out using a 1 wt. % aqueous KOH solution with 5 vol. % isopropanol at 70 °C for 20 min. This was followed by cleaning in HCl and a final dip in dilute HF prior to the diffusion process. A heavily doped n+ emitter was realized by diffusion at 920 °C using a liquid $POCl_3$ source, leading to a sheet resistance of 45□/Sq. The wafers were then metalized by screen-printing and firing in an infrared belt furnace diffusion, of an Ag grid contact on the front side and a full Ag/Al contact on the back side.

The total cell area was ~20 cm^2. Formation of the porous layer was accomplished by dipping the finished solar cells in a HF (48 wt %)-H_2O_2 (30 wt%)-ethanol (EtOH) mixture at room temperature without any protection to the metal contacts. The etching time was varied from 3 to 7 sec.

Morphology of the silicon surface after the treatments was examined by a Philips XL30 ESEM-FEG scanning electron microscope (SEM) equipped with an X-ray energy dispersive detection system (EDS) for the elemental analysis of the porous surface. The total reflectivity measurements were carried out in 300-1200 nm wavelength range with a Varian Cary 500 UV-Vis-NIR spectrophotometer equipped with an integrating sphere.

The PL from the porous solar cell was measured at room temperature using an UV light (325nm) from a Xenon lamp as the excitation source from a Perkin-Elmer LS-50B luminescence spectrometer. Spectral response and external quantum efficiency measurements were done in the wavelength range 350-1100 nm.

The measurement set-up consists of a Jobin-Yvon H25 monochromator with a tungsten filament lamp having an incident power of 170 W under PC control. The photovoltaic characteristics of the solar cells were obtained from illuminated $I-V$ measurements using a solar simulator under standard terrestrial conditions (AM1.5G, 100 mW/cm^2).

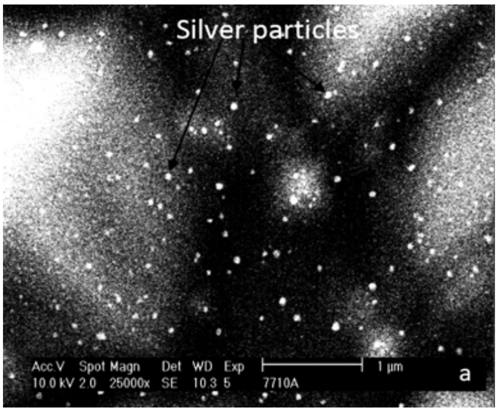
3. RESULTS AND DISCUSSION

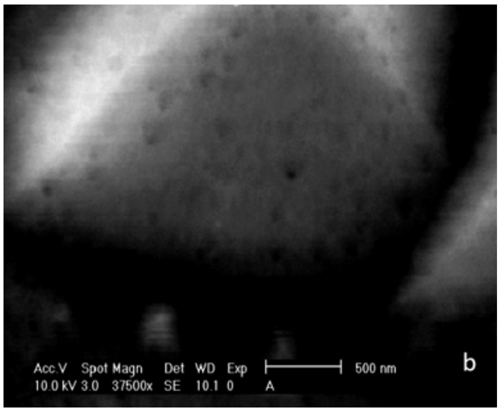
As reported in a previous study [10], the solution composition and etching time are crucial parameters that permit the partial dissolution of the front electrode which produce silver nanoparticules, then act as catalytic sites for PS layer formation, with a large distribution of silver particles on the surface.

Fig. 1a. shows a top view SEM micrograph of a porous film formed on a textured silicon solar cell. The texture surface has straight square pyramids of height 1 – 2 µm.

The surface of the pyramid facet contains micro pores that make the PS layer, with a diameter in the range 15 - 80 nm, Fig. 1b.

The EDX analysis, shown in Fig. 1c. confirms that the nanoparticles are silver and come from the partial dissolution of the front electrode during etching. SEM investigations show suitable structure for light trapping and diffusing.





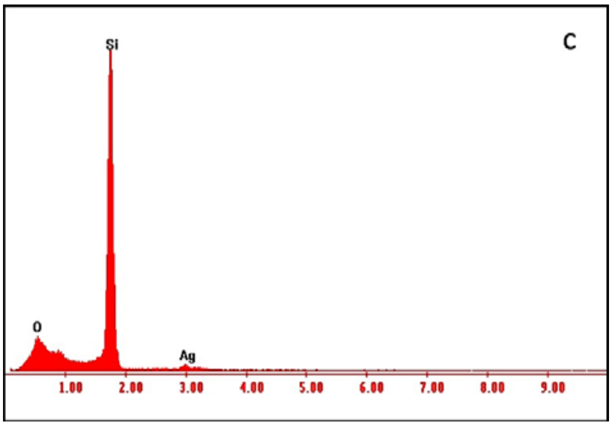


Fig. 1: SEM micrograph of PS layer formed on textured monocrystalline p-type Si wafer, (**a**) showing the presence of silver particles, (**b**) EDX spectrum of the silver particles, (**c**) magnified image of the PS-treated surface

The variation of the total reflectivity of the solar cells subsequent to various surface treatments is shown in Fig. 2. The reflectivity of a <1 0 0> oriented Si wafer after random pyramid texture is nearly constant in 500 – 1000 nm wavelength range, from 15 to 20 %.

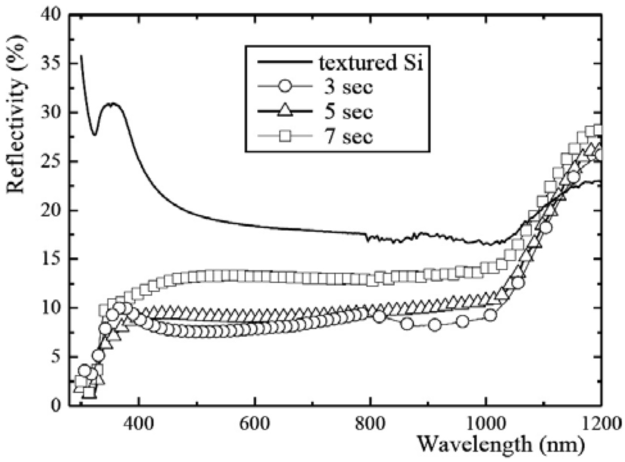


Fig. 2: Reflectance spectra for PS layers after etching in HF-H_2O_2-Ethanol for different etching durations varying from 3 sec to 7 sec.

Higher reflectivity values are obtained for $\lambda < 500$ and $\lambda > 1000$ nm. Application of an ARC on the textured Si wafer reduces the reflectivity for all wavelengths below 1000 nm [7, 13].

PS layers of suitable thicknesses have also been used as single layer ARC on Si solar cells having textured or polished front surface [14, 15]. Reflectivity is less than 10 % at any value in $400 < \lambda < 1000$ nm range for etching duration less than 5 sec.

Minimum reflectivity is observed for $t_e = 3s$. It is noted that for $\lambda < 450$ nm, R_λ is < 10 % for all PS layers except the one corresponding to the growth duration of 7 s.

For effective down conversion, the reflectance of the cell for higher energy photons should be minimal at the same time the overall weighted reflectance should also be minimal [16].

The photoluminescence measurements were carried out on the solar cells with 45 Ω/Sq sheet resistance. The etching times were 3, 5 and 7 sec.

Photoluminescence emission spectra of the PS layers for different etching durations are shown in Fig. 3. The PL spectra exhibit a broad band centered at 630nm. For comparison, PL spectrum of the reference cell (without PS layer) is shown. When the etching duration is less than 3s, there is no significant PL emission. As etching duration is increased, PL intensity and reflectivity both increase.

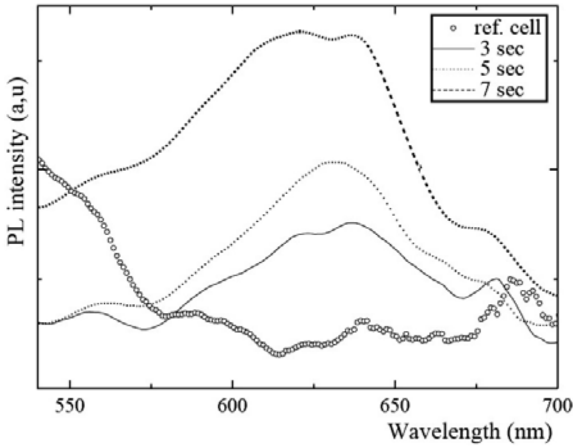


Fig. 3: Photoluminescence emission spectra of PS layers for different etching durations varying from 3 sec to 7 sec. The reference is untreated c-Si

As mentioned above, this PL reemitted as red light by the PS layer will reach the active region of the PN junction, thus increasing the solar cell photocurrent. The increase in the short circuit current density would essentially be due to an increase in light absorption (decrease of the reflectivity) and increase of the light path inside the active material owing to the diffusing character of PS and due to a non-negligible passivating role of the PS layer.

In order to separate the modified reflectivity of the PS layer from other effects such as better transmission of the light or a surface passivation, the external (eQE) and the internal quantum efficiency (iQE) of the solar cells A, B and C etched for 3, 5 and 7 sec respectively are plotted in Fig. 4.

The iQE is obtained from eQE and reflectance measurements according to the following equation:

$$\mathrm{iQE} = \frac{\mathrm{eQE}}{(1 - R_\lambda)} \tag{1}$$

where R_λ is the reflectivity.

It is clearly seen that sample C corresponding to a 7 sec. etch has the highest and best response. An increase in eQE is observed in the region of high energy photons.

After correction, the iQE of this cell is raised over the entire wavelength range compared to the two others. This means that the change in the reflectivity of the PS layer is not the only effect which determines the photo response after formation of a PS layer.

The increase in photocurrent is attributed mainly to three effects associated to the PS layer: ▪ improvement of the antireflection properties, ▪ passivation of the frontal side of the cell which is expected to be observable only in the short wavelength region, ▪ effect of the photo luminescent properties of the PS which could produce photo conversion of the high energy solar radiation into lower energy radiation thus enhancing the production of charge carriers and hence the solar cell conversion efficiency [17].

It can be inferred from the data above, Fig. 3 and Fig. 4, that the incident high energy photons ($\lambda < 500$ nm) are transformed via its room temperature PL, to red photons (namely 630 nm) which are absorbed in the silicon solar cell.

This leads to an increase in the carrier collection probability in the region where the conversion appears. As the PL intensity of PS increases, the resulting improvement in spectral response is recorded.

There is no straightforward reason to explain the increase of internal QE at longer wavelengths. The modification of the optical confinement of light and the elimination or decrease of some surface impurities and defects following PS formation may be the major contributing factors.

Measurements of output electrical characteristics of the solar cell before and after formation of PS were carried out under AM1.5 global spectrum.

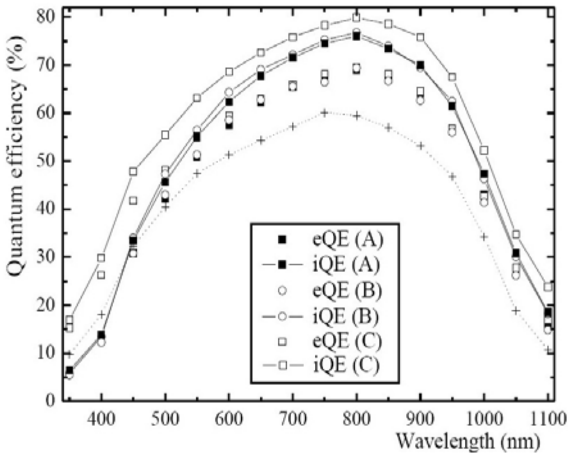


Fig. 4: Internal and external quantum efficiencies of Si solar cells after formation of a PS front layer for 3 sec (cell A), 5 sec (cell B) and 7 sec (cell C)
The spectrum of a reference cell, without PS, is also shown for comparison (dot line).

In solar cell A, there was an increase in short-circuit current density, J_{sc} of 18 %. In solar cell B, the increase in J_{sc} was of 20.6 % and for solar cell C, J_{sc} increases by 21.1 %.

When the PS layer is formed, a reduction of the dead layer may be observed leading to an enhancement of the current density, this change contributes efficiently to the improvement of iQE in the 400 - 700 nm spectral range. The enhancement of iQE in the 700-1100 nm spectral range of the base region could be due to the light diffusing nature of the PS layer.

This change in J_{sc} corresponds to additional photons contributing to the short circuit current. This increase in photon generated short circuit current density may be attributed to down conversion of higher energy photons into lower energy photons by photoluminescence resulting in efficient absorption in the solar cell [18].

It is obvious that PS treatment is done at the expense of the n^+ zone which may lead to thinning the dead layer of the emitter and its passivation quality. The PS-based textures reduce reflection loss and could substantially increase the cell's effective optical thickness by causing light to be trapped within the cell by total internal reflection.

The minority carriers' diffusion length is one of the most important electrical parameters used in photovoltaic's to quantify the optoelectronic quality of materials under study.

To clarify some aspects related to the influence of the PS layer on the solar cell parameters, **Table 1** shows the diffusion length calculated from the iQE spectra according to models exposed in the literature [19]. From the iQE spectra, it is observed that there is a gradual decrease of the measured photocurrent in the long wavelength range ($\lambda > 850$ nm) for all the three types of test devices.

Table 1: Diffusion length (L_n) measured by the analysis of the internal quantum efficiency for untreated Si solar cell and for the three different PS-treated Si cells

	Average diffusion length (µm)
Reference cell	193
Solar cell A	216
Solar cell B	236
Solar cell C	256

It may originate from the fact that absorption coefficient is lower at longer wavelengths; thereby resulting in a reduction in current collection efficiency in the long wavelength range. This trend in carrier photocurrent with the absorption coefficient ($\alpha_\lambda{}^{-1}$) due to the weaker absorption can be used to estimate the diffusion length in the near-band gap radiation (850 nm < λ < 1050 nm) by using the relationship between the iQE^{-1} and $\alpha_\lambda{}^{-1}$ accordingly [19, 20].

$$\frac{iQE}{f_0} - \frac{\alpha_\lambda}{L_n} = 1 \tag{2}$$

where L_n is the bulk diffusion length and α_λ is the absorption coefficient of the silicon corresponding to the wavelength λ and f_0 corresponds to the correction factor for non-uniform illumination of light.

The resultant diffusion length increases for the PS cells compared to the reference cell, on the one hand and increases with the etching time on the other hand. The improvement of the internal quantum efficiency is due to an increase of the minority carrier diffusion length [21].

Due to scattering by the PS layer, the light direction becomes oblique so that the light path is longer than that in a flat cell. The lower energy photons have a lower absorption coefficient; their light paths are still longer. The most part of the additional path is in the base region.

A PS cell generates more minority carriers in the base region. The results are indicative of the possibility of substantial enhancement of the diffusion length of PS stain-etched Si-based solar cells.

4. CONCLUSION

Metal-assisted etching in HF-H_2O_2-Ethanol has been applied to generate a PS ARC on textured monocrystalline silicon solar cells. The effectiveness of porous silicon as a down converting material for solar cells is clearly demonstrated and is easy to integrate in conventional manufacturing technology.

We have shown that implementation of the porous layer as down converter enhanced the iQE of standard silicon solar cell. The improvement is detected in the region where the nano structured silicon is excited (300 – 500 nm). The high energy photons are converted via the porous silicon PL to a quite strong visible red light (centered at 630 nm).

Such red photons produce electron-hole pairs that are collected more efficiently and increase the carrier collection i.e. short circuit current through the silicon solar cell. Increase in short circuit current density of 21 % in PS layer solar cell has been observed despite the lower antireflective properties that depend on etching time.

The reflectivity of the photo luminescent layer increases with increase in the etching duration. A short dip of 7 sec was sufficient to increase the photocurrent by 21 % without contact deterioration.

One important point related to the photon-down conversion effect is the fact that no shallow junctions are necessary for the solar cell structure since the high energy photons are converted into red photons which reach the active region of the junction.

From the point of view of solar cells applications, photoluminescence can be used for the improvement of efficiency in silicon solar cells.

Photoluminescence can serve in the photon-down conversion process transforming the high energy-photons into lower-energy ones, in the range of red wavelengths, permitting an easier absorption by the silicon substrate and improving the cell's performance at high energies, which are usually lost by thermalization processes in conventional solar cells.

Thus, we found that the improvement of the internal quantum efficiency is accompanied by an increase of the minority carrier diffusion length by more than 60 μm.

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