Plasma nanotexturing of silicon surfaces for photovoltaics applications: influence of initial surface finish on the evolution of topographical and optical properties

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Abstract

Using a plasma to generate a surface texture with feature sizes on the order of tens to hundreds of nanometers (“nanotexturing”) is a promising technique being considered to improve efficiency in thin, high-efficiency crystalline silicon solar cells. This study investigates the evolution of the optical properties of silicon samples with various initial surface finishes (from mirror polish to various states of micron-scale roughness) during a plasma nanotexturing process. It is shown that during said process, the appearance and growth of nanocone-like structures are essentially independent of the initial surface finish, as quantified by the auto-correlation function of the surface morphology. During the first stage of the process (2 min to 15 min etching), the reflectance and light-trapping abilities of the nanotextured surfaces are strongly influenced by the initial surface roughness; however, the differences tend to diminish as the nanostructures become larger. For the longest etching times (15 min or more), the effective reflectance is less than 5 % and a strong anisotropic scattering behavior is also observed for all samples, leading to very elevated levels of light-trapping.

1. Introduction

Despite significant improvements in the efficiency of competing technologies, crystalline silicon (c-Si) solar cells are leading the market in the photovoltaic industry, benefiting from high reliability, improving production module efficiencies, and continuing cost reduction. The best experimental cell results to date have shown an efficiency of 26.3 % [1], although the theoretical limit is 29.4 % [2]. Further improvements are still expected due to the implementation of new technological concepts. In particular, continuous efforts have been made to reduce the optical reflectance of the front surface of c-Si solar cells. Indeed, due to

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the high refractive index of c-Si at the wavelengths of the solar spectrum, the front-surfaces of c-Si cells must be textured and covered with antireflection coatings (ARC) in order to avoid elevated reflection losses. A standard technique to texture monocrystalline silicon at the microscale is chemical etching with KOH, NaOH, or tetramethylammonium hydroxide (TMAH) [3]. The reflection of light from the cell is reduced due to multiple reflections between topographical features of the front surface. This effect is mostly effective for normal incidence light rays, as will be discussed later, and still requires the addition of an ARC to further reduce the reflectance. The performance can be further improved through techniques producing textures at the nanoscale. Indeed, it has been shown that nanotextured silicon surfaces, depending on the shape and size of the structures, may exhibit very low reflectance without the need for an ARC layer [4]. Such surfaces are commonly called “black silicon” due to their visual appearance [5].

Ongoing investigations continue to focus on several techniques that produce nanotextured silicon surfaces: metal-assisted chemical etching [6–8], colloidal lithography [9], femtosecond laser texturing [10,11], and plasma texturing [12–14]. For high efficiency, low cost c-Si solar cells, plasma assisted texturing appears to have significant advantages, notably the ability to process large area, thin wafers (thickness below 100 μm) on a single side, with reduced silicon removal.

Plasma-assisted c-Si nanotexturing is typically obtained with an SF₆/O₂ discharge in a reactive ion etching (RIE) reactor [5]: more precisely, fluorine radicals are responsible for the etching of Si at the surface, while the addition of oxygen to the plasma enables the formation of in-situ micro-masking species of type SiOₓFᵧ responsible for the spontaneous formation of nanostructures. These species are in turn physically etched by ion bombardment [15,16]. Since SiOₓFᵧ species are highly volatile at room-temperature [17,18], the in-situ micro-masking is more efficient at cryogenic conditions [5]. However, black silicon can also be obtained at higher (room) temperature, although the suitable process conditions are more restrictive [19] and can benefit from the addition of other gases [20]. Nanotextured silicon surfaces obtained by plasma processing typically consist of needles or cones (base widths ranging from 30 nm to 500 nm). An efficiency of 22.1 % has been reported with solar cells having black silicon surfaces with an Al₂O₃/SiNx passivation stack on the front and interdigitated contacts on the back [12].

In a realistic industrial manufacturing process, the substrates would possess an initial surface microtexture due to the wafer manufacturing processes, usually induced by sawing, and then altered by saw damage removal steps. The influence of this initial surface finish on the front surface plasma nanotexturing and on the final optical properties of the processed wafer is not known.

In this work, we investigate the influence of the initial roughness of wafers on the nanostructure formation during the SF₆/O₂ plasma texturing. Since their formation occurs by in-situ micro-masking, we expect the presence of initial microstructures to alter the appearance and growth of the nanostructures. Hence, the evolution of the surface morphology during the etching is first characterized. Secondly, the optical properties of the etched surfaces are studied using measurements of the hemispherical reflectance at normal
incidence combined with the angular distribution of reflected light. Finally, absorptance measurements at normal incidence giving information about light-trapping improvements enabled by nanotexturing are studied. Values of photogenerated current densities are calculated and studied as a function of the angle of incidence. Results show that improvements of light management in silicon solar cells from front surface nanotexturing depend upon the initial surface roughness.

2. Experimental and theoretical approaches

2.1 Studied substrate finishes and nanotexturing process

Monocrystalline silicon samples consisting of 2 cm × 2 cm pieces of n-type wafers with (100) orientation with a resistivity of 4.5 Ω.cm were used in this study. The wafers, either grown by the Czochralski (CZ) or Float-Zone (FZ) method see Table 1, were purchased from different manufacturers and chosen for their four types of initial finish: slurry wire sawn (SWS), diamond wire sawn (DWS), double-side mirror-polished (DSP), and lapped (LPD) wafers. SWS and DWS wafers are used “as-cut”, i.e., they did not experience any other process after sawing from the ingot, and their surface properties differ according to the sawing technique employed [21]. On the other hand, DSP wafers underwent several mechanical and chemical etching processes inducing a very low surface roughness and a mirror-like visual appearance. Finally, LPD wafers underwent mechanical lapping with a slurry solution, followed by a chemical etching to remove the subsurface damage induced by the lapping process. These four types of samples have been chosen for the diversity of surface topographies.

The samples have been processed in a capacitively coupled plasma (CCP) system (Nano-master NRE-3500 [22]) for reactive ion etching (RIE). All the samples are processed with the same recipe with good reproducibility and homogeneity, for etching times between 2 min and 75 min. For each etching time, all of the samples were laid, unfixed on the electrode and simultaneously processed. The SF$_6$:O$_2$ volume flux ratio is 1.3:1, the total volume flux is 140 cm$^3$min$^{-1}$ (at 20 °C and 101 kPa), the pressure is 4 Pa, and the measured CCP power density is 0.17 Wcm$^{-2}$. The substrate electrode is water-cooled and kept at approximately 300 K.

All samples have a similar initial surface finish on each side, and only the side exposed to the plasma is modified during the process. A single run (with one of each substrate type) was performed for each process condition, so the data presented in this work represent typical results.

In order to compare optical properties of plasma nanotextured surfaces to typical commercial solar cells, an additional silicon sample (Pyramid+ARC) was added to the study. The latter has first been etched in an alkaline solution in order to obtain a pyramid texturing, and then coated on the front side by physical vapor deposition of an 80 nm thick indium tin oxide anti-reflective layer.
2.2. Optical characterizations

Hemispherical reflectance as well as absorptance has been measured for wavelengths $\lambda$ between 250 nm and 1250 nm, with a PerkinElmer Lambda 950 spectrophotometer equipped with an integrating sphere. The absorptance has been measured by placing the sample inside the integrating sphere with a variable angle center-mount sample holder.

In order to quantitatively compare the reflectance of the samples, the effective reflectance, $R_{\text{eff}}$, is computed, Eq. (1), by integrating the reflectance spectrum $R(\lambda)$ and weighting it by the AM1.5g solar spectral irradiance according to the ASTM G173-03(2012) standard [23]:

$$R_{\text{eff}} = \frac{\int_{280\text{nm}}^{1000\text{nm}} R(\lambda) S_{\text{AM1.5g}}(\lambda) d\lambda}{\int_{280\text{nm}}^{1000\text{nm}} S_{\text{AM1.5g}}(\lambda) d\lambda}$$

The upper limit at 1000 nm is chosen to cut off the contribution in the region where silicon is partially transparent. Beyond this wavelength, multiple reflections can occur inside the material. Thus, $R_{\text{eff}}$ is most representative of the external reflectance of the top surface. Similarly, in order to compare absorptance of the samples, the photogenerated current density $J_{\text{ph}}$ has been computed, Eq. (2).

$$J_{\text{ph}} = \frac{e}{hc} \int_{280\text{nm}}^{1200\text{nm}} A(\lambda) \lambda d\lambda$$

where $e$ is the electron charge, $h$ is the Planck constant, $c$ is the speed of light, and $A(\lambda)$ is the measured spectral total absorptance.

3. Results and discussion

3.1. Evolution of the surface morphology

Scanning electron microscopy (SEM) images, obtained with a Hitachi S-4800, of the initial surface morphologies are shown in Fig. 1 (left column). SWS and DWS wafers both exhibit micrometer-sized mounds and grooves with sharp edges. Whereas SWS wafers seem to have a nearly isotropic microstructure, DWS wafers show strong anisotropy corresponding to saw marks, characteristic of diamond wire sawing and observable with the naked eye. In contrast, LPD and DSP wafers are smooth: no structure can be detected by SEM for DSP wafers, while LPD wafers exhibit shallow pits with square edges dispersed on the surface with no observable long range order. Confocal microscopy measurements show that the root-mean-square (rms) roughness of the SWS and LPD wafers is around 0.8 $\mu$m, while a value of 0.3 $\mu$m has been measured for DWS wafers. The initial topography of DSP wafers has not been characterized through this method.

Samples of all four types of wafers were then nanotextured. Multiple processing times were used in order to gain insight into the formation of the nanostructures and the effect of the preexisting micro-morphology on their evolution. Chosen values for the process times are 2
min, 5 min, 10 min, 15 min, 30 min, and 75 min. SEM images of the processed samples are shown on Fig. 1. It can be seen on the inset images on Fig. 1 for nanotextured LPD samples that the nanostructures resemble cones, with an apex angle of roughly 45° (determined from side-view SEM images, not shown here).

Nanostructures appear rapidly after the beginning of the plasma process (nanostructures are already observed after only 2 min, images not shown here). The typical nanostructure size then continuously increases with processing time. They develop by etching the surrounding c-Si, so the resulting nanostructures are the negative shape of the etched volume. On DSP wafers, where the initial roughness is very low, the nanocones are vertically oriented and uniformly distributed. In contrast, nanostructure formation on SWS and DSP wafers is clearly influenced by the initial roughness; a less uniform distribution of sizes and slopes can be observed. Moreover, in deep grooves on SWS wafers, the growth of nanostructures seems to be hindered. On DWS samples, nanocones are aligned along the grooves, and they appear larger on the top of the grooves than on the bottom. Finally, it is noted that the shapes of the nanostructures become more complex as the processing time is increased. In particular, the cone-like structures seen after 15 min of etching exhibit multiple ridges on their sides.

Although grayscale top-view SEM images do not provide feature height, they can still provide estimates of the nanostructure lateral dimensions. In particular, it can be seen in Fig. 1 that the nanostructures are closely packed on the surface. The characteristic distance between nanostructures has been determined from the normalized and circularly averaged radial autocorrelation function (ACF) [24] computed from the grayscale SEM images. A typical example is shown in Fig. 2(a) as a function of the radius \( r \). The estimated pseudo-period \( \Lambda \) correspond to the location of the first local minimum of the ACF as seen on the example of Fig. 2(a) where a value of \( \Lambda \) is here numerically determined by fitting the ACF in the region near the minimum to a cubic polynomial in order to reduce the contribution of noise. Furthermore, SEM images show that there is a distribution of structure sizes on the surface, and therefore the pseudo-period \( \Lambda \) only represents an average nanostructure width.

Figure 2(b) shows the evolution of \( \Lambda \) with etching time for the four different initial surface conditions. The pseudo-period \( \Lambda \) can be seen to be significantly less than the wavelengths of interest for photovoltaic applications (roughly between 280 nm and 1100 nm) for etching.
times below 30 min. As shown in Fig. 2(b), \( \Lambda \) depends very little on the initial surface finish of the wafer. After 2 min of etching, \( \Lambda \) is about 23 nm ± 3 nm for all samples, and it increases with etching time following a scaling law \( \Lambda \propto t^\gamma \), where \( t \) is the etching time and \( \gamma \) is an exponent. Comparable behaviors have been observed by several teams for silicon surface roughening induced by plasma processes with SF\(_6\) [25,26], CF\(_4\)/O\(_2\) [27], and Cl\(_2\) [28]. Note that the computation of \( \Lambda \) is influenced by the presence of the initial microstructure, especially on SWS wafers, once the size of the nanostructures induced by RIE is of similar scale. This effect is most likely responsible for an overestimation of \( \Lambda \) for the SWS sample etched for 30 min. For the DSP samples, where the initial roughness is negligible compared to the scale of the RIE induced textures, a value of \( \gamma = 1.3 \pm 0.1 \) is found (all stated uncertainties represent 95% confidence limits).

The dynamic evolution of nanostructures is intimately linked to their formation mechanism. While etchant reemission has been suggested as a possible cause for roughening [27], other experimental investigations support a mechanism linked to the formation of a passivation layer, e.g., “soft” etch-inhibitors such as SiO\(_x\)F\(_y\) species [29,30], as previously mentioned, or to the presence of “hard” etch-inhibitors due to contamination from the reactor redepositing on the silicon surface [26]. A recent study [31] successfully simulated the empirical dynamic evolution of black silicon by considering the formation of a passivation layer and the balance between its growth and etch rates. However, the observed scaling behavior is insufficient to definitively assess the nanostructure formation mechanism.

Nevertheless, the similar trends observed in Fig. 2(b) for all types of samples show that the initial topography on these samples has little impact on the length scales of the nanostructures. However, the initial microstructure of the SWS, DWS, and LPD samples is still observable in the SEM images of the samples for etching times below 30 min. A dual-scale structure is present and will affect their optical properties.

### 3.2. Evolution of the optical properties

#### 3.2.1. Total reflectance

The reflectance of the initial c-Si samples surfaces is strongly influenced by the surface roughness and crystalline structure. Figure 3 shows the reflectance spectra of the substrates before etching, together with the theoretical Fresnel reflectance for a planar surface [32] and the AM1.5g solar spectrum [23]. DSP and LPD wafers exhibit similar reflectance from 250 nm to 1000 nm. Their effective reflectance \( R_{\text{eff}} \) is high (37.8 % and 35.8 % for DSP and LPD, respectively) due to their very low surface roughness. The rise of reflectance for wavelengths longer than approximately 1 \( \mu \)m is due to the substrate becoming semi-transparent: part of the light entering the silicon can escape it after being reflected at the rear surface.

Unetched DWS wafers, despite their high surface roughness, exhibit a comparable level of reflectance \( (R_{\text{eff}} = 37.4 \%) \) as the unetched DSP and LPD samples, except for wavelengths below 450 nm. Indeed, the peaks at about 270 nm and 360 nm, corresponding to the Van Hove singularities in the density of states of crystalline silicon [33], do not appear. The lack of Van Hove features is attributed to a thin layer (a few nanometers) of amorphous silicon on top of the c-Si, induced by plastic ductile mode cutting during diamond wire sawing, which mechanically hardens the c-Si surface [34].

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In contrast, the characteristic peaks of c-Si are observed for SWS wafers, but the whole spectrum is shifted to lower values of reflectance, with $R_{\text{eff}} = 21.6\%$. This shifting of the entire reflectance spectrum is attributed to light trapping; the large topographical features found on the surface cause multiple reflections to occur.

Figure 4 shows the evolution in the reflectance spectra of the four sample types during etching. The reflectance of the front surface of the silicon samples strongly decreases with the formation of nanostructures. The optical properties of nanotextured surfaces are often interpreted in terms of either an effective medium effect or a multiple reflection effect [35]. For normal incidence, the effective medium effect applies when the lateral size of the nanostructures, which can be taken here to be the pseudo-period $\Lambda$, is much smaller than the scaled wavelength $\Lambda/n_{\text{Si}}$ ($n_{\text{Si}}$ is roughly 3.5 to 4 through most of the wavelength range of interest). In this case, the black silicon layer acts as an intermediate layer of graded refractive index between air and silicon [36]. On the other hand, the multiple reflections effect applies if the wavelength of the incident light is much smaller than $\Lambda$. This phenomenon can be understood by geometrical optics: rays of light impinging the surface are scattered several times between the structures, so that a larger fraction of incident light is transmitted into the silicon. This latter effect also explains the low initial reflectance of SWS wafers, as previously mentioned. In the case of the RIE processed samples, the pseudo-period $\Lambda$ of the nanostructures lies between the two limiting cases, and diffraction phenomena have to be taken into account. Moreover, the pseudo-period $\Lambda$ estimated for the samples is only an average value and does not represent the whole distribution of sizes, making the analysis of the broadband anti-reflection properties of the nanotextured surface more difficult as well.

However, some qualitative trends can still be understood by the effective medium or multiple-reflection effects. Indeed, for the samples processed 2 min or 5 min and where $\Lambda < 100\,\text{nm}$, the effective medium effect qualitatively explains the decrease of reflectance in the whole spectrum. For the reflectance spectra shown in Fig. 4, it is clear that the reflectance reduction of samples etched for 2 min and 5 min is stronger for shorter wavelengths, consistent with a simple effective medium layer. For the samples etched longer, a graded index is necessary to describe the results. Indeed, in order for the effective medium layer to smoothly adapt the refractive index, its depth should be of the order of magnitude of the wavelength [37]. It should be noted that the initial decrease of reflectance and reappearance of the Van Hove features observed for the DWS samples in the whole range of wavelengths just after 2 min etching is attributed to the removal of the thin amorphous silicon layer which covered the surface, as previously discussed.

For samples processed 10 min or more, diffraction phenomena have to be taken into account, and iridescence is actually observable on some samples. Finally, for samples etched for 30 min or 75 min, the pseudo-period reaches the micrometer scale, so that for short wavelengths multiple-reflections can occur, and the small recovery of reflectance in this part of the spectrum might be explained by enhanced retro-reflection from these large structures [38]. After 75 min etching, the reflectance is similar for all the samples between 250 nm and 1100 nm, with a root mean square reflectance difference below 1% between any pair of
samples, showing that the influence of the initial microscale roughness on the hemispherical reflectance has vanished.

The effective reflectance, $R_{\text{eff}}$, is computed in order to compare all the samples. By weighting the reflectance with the AM1.5g solar irradiance spectrum, this single parameter characterizes the average decrease of reflectance achieved from nanotexturing that is relevant for photovoltaic applications. As previously discussed, the lateral size of the nanostructures is of primary importance to interpret the effect of nanotexturing on the reflectance. Figure 5 shows the evolution of $R_{\text{eff}}$ as a function of the pseudo-period of the nanostructures. $R_{\text{eff}}$ already decreases by 7% to 20% (relative) when nanostructures have a pseudo-period of about 23 nm (corresponding to only 2 min of etching). More interestingly, $R_{\text{eff}}$ drops by 90% (relative) as $\Lambda$ approaches 150 nm. Afterwards, as the etching continues, the nanostructure pseudo-period continues to increase, but $R_{\text{eff}}$ stays stable with a value between 2% to 3% for all of the samples. Since $R_{\text{eff}}$ integrates the reflectance over a wide range of wavelengths, a direct interpretation of the threshold value for $\Lambda$ of around 150 nm is difficult. However, this value gives an estimate of the nanostructure size that should be produced in order to obtain an efficient anti-reflection effect over the entire relevant solar spectrum.

3.2.2. Directional reflectance—Measurements of angle-resolved diffuse scattering were also performed on most of the samples. The bidirectional reflectance distribution function (BRDF, $\Omega$), quantified as the radiance scattered into a specific direction normalized by the incident irradiance [39], was measured using 633 nm radiation at an incident angle of 5° and scanning directions evenly spaced in a directional cosine space centered on the surface normal [40,41]. Figure 6 shows the results of these measurements. Each of the surfaces has a distinctive scatter pattern prior to any etching. For the lowest etching times, the DSP sample had a BRDF that was below the instrument noise floor, as the instrument was configured, except near the specular direction. One of the samples was not measured for this reason, and the measurements for the 5 min samples are not shown here. The SWS sample had a relatively uniform BRDF, the DWS sample shows a distinctive diffraction pattern from the wire saw marks at approximately 45° to the (110) crystal direction, and the LPD sample showed a distinctive four-fold symmetric pattern that was correlated to a large number of {113} surface planes.

As the samples are etched, their scatter patterns evolve towards a common behavior: while remnants of their original structure are still observed after 15 min, their behaviors remarkably converge for 30 min of etching. The scattering from the SWS samples remain uniform but decrease in value. The diffuse part of scattering from the DWS samples decreases, while the distinctiveness of the saw mark diffraction is reduced. The scattering from the DSP and LPD samples rise in directions having low initial scatter, while the distinctiveness of its original scattering pattern is reduced. The DSP samples continue to exhibit specularity until 15 min of etching, albeit much reduced from that of the unetched surface, and totally disappears after 30 min.

3.2.3. Absorptance and Light Trapping—Figure 7 shows absorptance spectra measured at normal incidence for the initial and nanotextured SWS and LPD samples, along
with the theoretical Yablonovitch limit for a 280 μm thick silicon substrate. Measurements have also been performed on a c-Si sample that has been pyramid textured in an alkaline solution and coated with an ARC (hereafter labeled Pyramid+ARC sample). The photogenerated current density $J_{ph}$ in the silicon substrate is also calculated from the absorptance spectra, Eq. (2), and given for selected samples in Table 2.

After 30 min etching, absorptance has almost reached its highest value over the full wavelength range for SWS and LPD samples, and the photogenerated current density reaches values around 42.8 mA/cm$^2$, close to the 43.9 mA/cm$^2$ theoretical value obtained from the Yablonovitch limit.

For wavelengths below 1000 nm, where silicon is highly absorbing, the gradual increase of absorptance with texturing time is mainly due to the decrease of reflectance at the front surface. On the other hand, above 1000 nm, enhancement of absorptance is mainly due to improved light-trapping inside the silicon. Above 1180 nm, some samples also show significant absorptance values exceeding the Yablonovitch limit: this phenomenon is attributed to free carrier absorption due to metallic impurities, likely originating from wafer slicing.

As the unetched LPD sample has rather poor light trapping, the improvements are particularly noticeable for LPD samples as they are etched. Indeed, for the spectra shown on Fig. 7(b), it is striking that the absorption by the LPD samples is much lower than by the SWS samples in the range 1000 nm to 1200 nm and for texturing times below 30 min. In the case of SWS samples, we have shown that the initial texture of both rear and front surfaces induces a high level of scattering, which is also preserved during the nanotexturing of the front surface, explaining a very good light-trapping for all the SWS samples. For LPD samples on the other hand, the poor light-trapping (samples etched between 0 min and 15 min) can be explained by a low level of scattering at both interfaces. However, for 30 min etched samples, the absorptance in the near infrared region is similar for SWS and LPD samples (see Fig. 7(c)), with a root mean square difference below 2 % between the two absorptance curves. That is, after 30 min etching, the scattering from the front surface becomes high enough so that light-trapping is effective even with a weakly scattering rear-surface. Therefore, absorptance measurements have shown that in order to achieve a high level of light-trapping on single-sided nanotextured wafers with a weakly scattering rear surface, the pseudo-period $A$ of the nanostructures should be at least 400 nm.

Absorptance measurements show that the constraint on etching time regarding light-trapping properties would be relaxed for double-side textured samples. Indeed, SWS samples can be considered double-side textured, with a front side nanotexturing and a rear-side microtexturing, and it is likely that similar optical results would be obtained if the back surface had been wet-textured [42].

An upper limit for the texturing process time will be set by the electrical properties of the nanotextured surface. Indeed, RIE processing of silicon induces defects such as impurities or vacancies [43] that will degrade the surface passivation level and, in turn, the open-circuit voltage of the cell [42]. In order to achieve good passivation, though, a damage removal
etching subsequent to nanotexturing might be applied [14,44], which will also improve the short wavelength response of the solar cell, since these wavelengths are absorbed at very shallow depths [45]. However, this additional step usually also induces a recovery of the reflectance over the entire solar spectrum due to a smoothing of the nanostructures.

3.2.4. Omnidirectional Absorption—Apart from strongly increasing absorptance at normal incidence due to a drop of hemispherical reflectance and to enhanced light-trapping near the bandgap, another benefit of using a nanotextured silicon front surface in solar cells is the good response to incident light at high angles [46,47]. From this property alone, an estimated 2% increase in total annual delivered energy is expected for a fixed panel installation for plasma nanotextured c-Si cells compared to pyramid textured cells [12]. In order to characterize this property, total absorptance spectra have been obtained as a function of angle of incidence, and photogenerated current densities have been computed and compared to the case of the Pyramid+ARC sample. Figure 8 shows the dependence of $J_{\text{ph}}$ on the angle of incidence for the SWS and LPD samples etched 30 min, compared to the Pyramid+ARC sample. The data shown in Fig. 8 have been normalized by their value at normal incidence. The absolute values of $J_{\text{ph}}$ for the various samples at normal incidence are given in Table 2. Note that the thickness of the samples varies.

For the Pyramid+ARC sample, the photogenerated current density steadily decreases as the angle of incidence increases, with $J_{\text{ph}}$ already dropped by about 5% at 40° angle incidence. On the other hand, $J_{\text{ph}}$ values for SWS and LPD nanotextured silicon samples remain above 98% of the normal incidence value for angles below 40°. $J_{\text{ph}}$ for the nanotextured samples remains higher than the Pyramid+ARC sample until the angle of incidence reaches about 70°. At 70°, the decrease is comparable for nanotextured and Pyramid+ARC samples, with a value of about 89% of the normal incidence value.

It should be emphasized that the front-side silicon surface must be coated with passivation layers to prevent recombination of carriers at the surface. In the case of nanotextured silicon, the best reported efficiencies have been obtained with atomic layer deposition (ALD) of aluminium oxide coatings [12]. ALD allows precise control of the layer thickness [48] and very good conformality on these surfaces [49]. This supplementary coating will modify the optical properties of the solar cell. In particular, as the refractive index of aluminium oxide lies between the indices of air and silicon, a decrease of reflectance is generally observed on aluminium oxide coated nanotextured samples [50,51]. The consequences of this additional layer on the light-trapping and high incident angle response have not been evaluated. It is expected that an optimal trade-off between high light absorption and low carrier recombination must be made. Further investigations are needed in order to optimize nanotextured silicon solar cells.

4. Conclusion

We have observed the evolution of topographical and optical properties of plasma nanostructured silicon surfaces with varying initial surface finishes. It has been shown that despite very different initial morphologies, the nanostructure lateral size $\Lambda$ is similar for all samples at any given time during the etching, and follows a scaling law with time, of type $\Lambda$
∝ tγ, with γ = 1.3 ± 0.1 (determined for DSP samples). This scaling law demonstrates a length scale selection during the etching, which is not affected by any pre-existing roughness at the microscale. In all cases, the nanostructures have lateral sizes on the order of tens of nanometers after 2 min etching, and reach the micrometer scale after 75 min.

Measurements of the BRDF at 633 nm and near-normal incidence, which are – to the best of our knowledge – reported for the first time for plasma nanotextured silicon samples, show the evolution in the distribution of reflected light during the nanotexturing and its dependence on the initial surface finish. In particular, when diffractive (for DWS samples) or specular behaviors (DSP and LPD samples) are initially observed, greater scattering behavior is observed after nanotexturing, and while the nanostructure size increases, the relative contributions of diffracted and specularly reflected light diminish compared to that of the scattered part.

Although initial optical response strongly depends on the surface finish, the evolution of the total spectral reflectance and absorbance during nanotexturing is similar for all the samples, and determined by the nanostructures’ (lateral) size. Two threshold values have been identified:

a. For nanostructures larger than approximately 150 nm, the measured effective reflectance of the surface plateaus at a minimal value of approximately 2% to 3% regardless of the initial surface finish, and good light-trapping (required to absorb near-bandgap photons) was obtained when the initial texture of the silicon surface induces sufficient scattering at the front or rear surface (as it has been observed for SWS samples).

b. For nanostructures larger than approximately 400 nm, both very good anti-reflective and light-trapping properties have been obtained regardless of the initial surface finish. The favorable light-trapping properties are attributed to a sufficient level of scattering at the front surface induced by nanotexturing itself. Angular dependent absorptance measurements on such samples have also demonstrated the improved behavior of nanostructured silicon for high-angles of incidence compared to a reference Pyramid+ARC sample, showing the possibility for increased delivered power in the case of fixed solar panels.

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Fig. 1.
Top-view SEM images of four types of sample without texturing (left column) and after various RIE etching times (2 min, 10 min, 15 min and 30 min). Inset images for the textured LPD samples are 40° off normal tilted views, magnified 3.5× compared to the corresponding top views.
Fig. 2.
(a) Typical example of radial autocorrelation function with corresponding SEM top-view image (DSP sample etched 10 min), and (b) evolution of pseudo-period of nanostructures, $\Lambda$, as a function of RIE etching time for the four sample types.
Fig. 3.
Reflectance spectra of four types of unetched sample, as well as theoretical Fresnel reflection at interface between air and c-Si. The AM1.5g solar irradiance spectrum is also shown with its scale on the right.
Fig. 4.
Evolution of reflectance spectra (from 250 nm to 1250 nm) of samples having undergone different RIE etching times.
Fig. 5.
Effective reflectance as a function of nanostructure pseudo-period for four types of sample.
Fig. 6.
BRDF, $f_r$, measured for four surface types and for five etching times. The data are shown in projected cosine space, and a grid (30° in polar angle and 45° in azimuth angle) is overlaid on top of the data. The black point in each data to the left of the surface normal is due to the detector blocking the incident beam. The incident angle was 5° and the wavelength was 633 nm. The samples are aligned so that the (110) crystal direction is horizontal.
Fig. 7.
Evolution of the absorptance spectra with RIE etching time for (a) the SWS and (b) the LPD samples. (c) Close-up comparison of absorptance spectra for 30 min etched SWS and LPD samples at near-bandgap wavelengths. The solid black curves show the theoretical Yablonovitch limit of absorptance for a 280 μm thick c-Si substrate.
Fig. 8.
Dependence of photogenerated current density on angle of incidence, normalized by value at normal incidence, for Pyramid+ARC sample and 30 min etched SWS and LPD samples. The value at 50° for the Pyramid+ARC sample is not shown due to retroreflection out of the entrance port of the integrating sphere.
Table 1
Labels and description of the samples used in this study.

| Label      | Surface finish (similar on each side) | Growth method | Wafer thickness (μm) |
|------------|---------------------------------------|---------------|----------------------|
| SWS        | Slurry-wire-sawn                       | FZ            | 275 ± 5              |
| DWS        | Diamond-wire-sawn                      | CZ            | 177 ± 2              |
| DSP        | Mirror polished                        | CZ            | 280 ± 2              |
| LPD        | Lapped                                | CZ            | 285 ± 5              |
| Pyramid+ARC| Pyramid texturing with anti-reflective coating | FZ            | 240 ± 5              |
Table 2

Photogenerated current densities $J_{ph}$ calculated at normal incidence for Pyramid+ARC sample, 30 min RIE etched SWS and LPD samples, and value for Yablonovitch limit. Uncertainties represent 95% confidence limits, for $J_{ph}$ they are estimated from uncertainties in the absorptance measurements.

| Samples             | Sample thickness (μm) | $J_{ph}$(mA.cm$^{-2}$) |
|---------------------|-----------------------|------------------------|
| Pyramid + ARC       | 240 ± 5               | 42.7 ± 0.2             |
| SWS – 30 min etching| 275 ± 5               | 42.8 ± 0.2             |
| LPD – 30 min etching| 285 ± 5               | 42.9 ± 0.2             |
| Yablonovitch limit  | 280                   | 43.9                   |