LETTER

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Letter

Sunlight-thin nanophotonic monocrystalline silicon solar cells

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Abstract

Introducing nanophotonics into photovoltaics sets the path for scaling down the surface texture of crystalline-silicon solar cells from the micro- to the nanoscale, allowing to further boost the photon absorption while reducing silicon material loss. However, keeping excellent electrical performance has proven to be very challenging, as the absorber is damaged by the nanotexturing and the sensitivity to the surface recombination is dramatically increased. Here we realize a light-wavelength-scale nanotextured monocrystalline silicon cell with the confirmed efficiency of 8.6% and an effective thickness of only 830 nm. For this we adopt a self-assembled large-area and industry-compatible amorphous ordered nanopatterning, combined with an advanced surface passivation, earning strongly enhanced solar light absorption while retaining efficient electron collection. This prompts the development of highly efficient flexible and semitransparent photovoltaics, based on the industrially mature monocrystalline silicon technology.

Main text

Pyramids have long been the dominant topography at the front surface of monocrystalline-silicon solar cells. These micron-scale random structures scatter the incoming light and thus improve the in-coupling and trapping of photons inside the silicon absorber [1]. Scaling the surface topography one order of magnitude down to the sunlight wavelength, earning nanophotonic structures, was first proposed for amorphous [2] and then for crystalline-silicon (c-Si) cells [3], at times when the price of polysilicon skyrocketed and the targets in cell thickness plummeted [4, 5]. Going ‘nano’ can reduce not only the silicon loss by texturing smaller structures, but also reduce the light absorption loss by playing with the wave nature of light. Absorption losses become particularly critical for thinner c-Si cells, which cannot absorb (near) infra-red photons in one-pass. Over time, a variety of concepts and techniques for nanostructuring have been investigated [6–8].

For thin c-Si cells, nanostructures are an ultimate challenge as the surface passivation becomes crucial, and as handling the fragile and flexible thin films poses severe constraints on processing. Consequently, the number of nanophotonic monocrystalline-silicon cells thinner than 10 μm reported in literature is limited. Such cells predominantly have an open-circuit voltage below 600 mV (with the marked exception of a back-contact cell [9]), showing the difficulty to reach good electrical performances [10–15]. They cover a large variety of architectures but mostly with high aspect-ratio nanostructures, such as nanowires or nanocolumns, that offer superior optical performance. The best energy-conversion efficiencies are however achieved with shallower
tapered textures, shaped as periodic nanocones [9] or periodic inverted nanopyramids [13, 14] that better preserve the electrical performances. Recent findings now indicate that disturbing the periodicity of these patterns could further improve their light trapping effect [16, 17]. Critically, the thin crystalline-silicon films were mostly produced by wafer thinning or from SOI wafers, thus with high silicon waste, except for plasma-enhanced chemical vapor deposition growth [14]. The potential development of thin-film monocrystalline-Si photovoltaics then not only relies on the electrical integration of nanophotonics, but also on the integration of kerf-less thin-film fabrication processes and of up-scalable nanostructuring techniques.

Here, the nanophotonic ultra-thin monocrystalline-silicon solar cell efficiently combines a kerf-less thin film method [18], a higher-absorption self-assembled nanotexture with amorphous order [19], with a robust surface passivation [20] and an optimal nanotexture integration [21]. This allows the scaling of the silicon thickness (830 nm) down to the sunlight wavelength, while boosting the optical performance (Jsc, short-circuit current) both for light in-coupling and light trapping without degrading the electrical performance (Voc, open-circuit voltage and FF, fill factor). Nanophotonics double the overall energy-conversion efficiency that reaches 8.6% (independently certified), i.e., higher [10, 12, 14, 15, 22] or comparable [11] to the substantially thicker (at least 10 times thicker) cells [9, 13].

The front surface of the initially micron-thin solar cell is textured with rounded inverse nanopyramids, the ‘nanocups’, that self-assemble with short-range order and are the result of a carefully engineered trade-off between photon and charge-carrier collection [18] (figure 1(a); see the methods section for the fabrication details of the kerf-less monocrystalline film [18] and the nanocups [19]). The nanocups are covered with standard hydrogenated amorphous-silicon (a-Si:H) serving as the passivating layer and heterojunction emitter. At the rear side, the c-Si is passivated by a dedicated thin layer of hydrogenated microcrystalline silicon oxide (µc-SiO₂:H) that fulfills multiple electrical and optical functions. The nanostructure and solar cell fabrication sequence is available in the supporting materials, figure S1 is available at stacks.iop.org/NANOF/1/021001.

The nanostructured surface is designed to simultaneously optimize the optical and electrical performances of the cell. Optically, earlier studies realized that a controlled disruption of periodicity of nanophotonic patterns, preserving short- or long-range order, improves the optical absorption in photovoltaics by spectrally and angularly broadening the nanopattern interference effects [16, 17, 23–26]. Here, the nanocups pattern is self-assembled by hole-mask colloidal lithography, where the electrostatic forces result in a short-range order, featuring a near-neighbor distance Gaussian distribution [19]. With a peak at ~580 nm and nanocups diameter of ~600 nm, it presents for this film thickness the best compromise between light in-coupling, associated with small near-neighbor distances, and light-trapping of low-energy photons, requiring larger pitches [27–29].

Further, the nanocup depth-profile is a rounded square-based pyramid with the aspect ratio (length by diameter) of 0.9–1 and, importantly, without negative slopes (atomic-force microscopy (AFM) scans can be found in the supporting materials, figure S2). Compared to steep slopes (i.e. squared depth-profiles, such as in cylindrical holes), gentle slopes provide a better antireflection, as the submicron topography realizes a progressive transition of the refractive indices from air to silicon [30, 31]. For the same reason, the pattern is etched with a high area filling-fraction of 85% (the ratio between the area covered by the holes and the total area), minimizing the flat surface area [23, 30] and by this reaches very low reflectance.

Furthermore, gentle slopes are the key for preserving the electrical performance of the cell since they ease the deposition and preserve the quality of the top layers (for surface passivation, antireflective coatings, and metal contacts), thus preventing degradation of the minority-carrier surface recombination velocity [29] or the sheet- and contact-resistances [32]. More aggressive profiles are allowed, in principle, provided that a perfectly conformal deposition technique such as atomic layer deposition is available [33, 34]. The average nanocup depth of ~530 nm, set by the diameter and the etching process, results in a surface area increase of 1.9 times, which is higher than with alkaline wet-etched pyramids (1.7 times), but still low compared to nanowires or nanocolumns. This effectively limits the charge-carrier losses by surface recombination.

Etching the nanocups at the front-side of the thin silicon film results in a considerable light absorption enhancement with a minimal material consumption. The absorption is boosted in a broad range of incidence angles (figure 1(c)), thanks to the graded-index effect of the nanoscale and to the disruption of periodicity by the self-assembled pattern [16]. The equivalent thickness d_eq of our nanophotonic silicon layer, initially 1.1 μm thick, defined as the thickness of a flat thin film with the same amount of material, reaches down to 830 nm. Nanophotonic patterns thus provide substantial waste reduction as compared to the several microns lost when etching standard micron-scale pyramids.

Thin (below 50 μm) crystalline-silicon films are notoriously challenging to process into solar cells. Since their minority-carrier diffusion length becomes comparable to the film thickness, they require excellent surface passivation, and since silicon films are fragile and lack rigidity, they require extensive process adaptations, particularly with the nanofabrication. We choose the anodic bonding of the thin c-Si film to glass, as glass offers good resistance and inertness during all process steps. Besides, anodic bonding is a direct bonding method that
avoids any interference from a gluing agent [35, 36], offering great adhesion despite its low temperature (200 °C–400 °C). The front nanophotonic surface is processed as a standard amorphous-silicon/crystalline-silicon heterojunction cell, coated with intrinsic (i) and doped (n⁺) a-Si:H as the passivation and emitter layers respectively, and a transparent conductive oxide as antireflective coating and contact layer. An a-Si:H heterojunction was chosen as it allows low temperature processing (“200 °C), as the n⁺ emitter is deposited on the nanotexture rather than diffused through it and as intrinsic a-Si:H provides excellent surface passivation. On the rear side, p⁺ doped µc-SiOₓ:H is used instead (figure 1(a)), as the a-Si:H passivating effect would significantly be reduced by the anodic bonding [20]. Besides, in a 1.1 µm thin cell, the a-Si:H passivation layer absorbs a significant amount of photons below 700 nm not only at the front- but also at the rear-side, since more than 60% of the photons beyond 520 nm are not directly absorbed and reach the rear side, inducing significant Jsc losses [18]. Doped µc-SiOₓ:H combines simultaneously efficient chemical and field-effect passivation, electrical conduction, and low absorbance to buffer the metal rear contact. The cell design thus combines an advanced rear-coating for surface passivation with a carefully crafted nanophotonic surface profile.

The J–V curves of the two best nanophotonic and flat cells demonstrate the doubling of the energy-conversion efficiency (figure 2(a)). Table 1 summarizes the cells performances for two tested a-Si:H emitter thicknesses. The nanophotonic surface optically boosts the cells and their Jsc approaches 20 mA cm⁻², while their electrical performance is remarkably preserved as evidenced by improved Voc and FF values. The process reproducibility was confirmed and the highest-performing cell was independently measured by ISE CalLab. The latter marked that the in-house J–V measurements overestimated the Jsc (as our calibration cell was not of...
similar type, but that the external quantum efficiency (EQE) measurements—which gives in function of wavelength the ratio between the number of electrons collected by the cell and the total number of incoming photons—were fully reliable.

A comparison with previously reported cells is not straightforward since all differ either in material, thickness or design (a review can be found in the supporting materials table S1). The present efficiency of 8.6% is independently confirmed and stands out for its high Voc and FF values, which is an indication of the successful nanotexture integration. In particular, we can draw the comparison to our own reported nanotextured cells [29] that featured nanocylinders with square sidewalls. In the present case, the successful nanostructure integration enabled improving the overall efficiency rather than the Jsc alone. The latter improved on average by 60%.

Absorption spectra and EQE show that absorption and Jsc improved due to simultaneously improved light in-coupling and light trapping (figure 2(b)). In-coupling can be visualized at shorter wavelengths, where most photons are absorbed in one pass (i.e. below 520 nm), and trapping impacts the longer wavelength photons reaching the rear-side mirror. The strong discrepancy between absorption and EQE points out that a significant part of the absorbed photons is lost for the charge-carrier collection at both sides of the spectrum. These losses have two origins: (i) charges can be lost from the photon absorption in non-active parts of the device, mainly at the rear-side mirror and the emitter; (ii) charges can be lost in the active material by surface and bulk recombination. As for (i), a large part of the photons are lost by absorption in the Al contact and in the ARC and emitter [29]. Parasitic losses at the front-side emitter may be partly reduced by depositing a thinner a-Si:H layer. Here, a 1.7 times thinner layer resulted in a gain of more than 1 mA cm\(^{-2}\) for nanotextured cells and 0.3 mA cm\(^{-2}\) for flat cells (table 1), yet without any impact on Voc. At the rear side, the parasitic absorption and recombination losses cannot be easily distinguished, as the presence of \(\mu c\text{-SiO}_x\text{H}\) improves both surface passivation and mirror reflectance [20]. An illustration of these parasitic losses on EQE can be found in the supporting material, figure S3. They are the main reason behind the wide gap between the Jsc (19.7 mA cm\(^{-2}\)) and the Lambertian limit (~34 mA cm\(^{-2}\)), as pointed out by Schuster et al [37]. They introduced a figure of

**Table 1.** J–V performance of the nanophotonic versus flat cells, processed with two different thicknesses of a-Si:H emitters (standard deviation in brackets).

<table>
<thead>
<tr>
<th></th>
<th>Number of samples</th>
<th>Number of cells</th>
<th>Jsc (mA cm(^{-2}))</th>
<th>Voc (mV)</th>
<th>FF (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nanostructured</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Best calibrated</td>
<td>1</td>
<td>1</td>
<td>19.72</td>
<td>560</td>
<td>78.2</td>
<td>8.64</td>
</tr>
<tr>
<td>Best</td>
<td>1</td>
<td>1</td>
<td>21.1</td>
<td>563</td>
<td>81</td>
<td>9.58</td>
</tr>
<tr>
<td>Average thin a-Si</td>
<td>3</td>
<td>23</td>
<td>20.5 (0.51)</td>
<td>558 (6.49)</td>
<td>75 (4.0)</td>
<td>8.60 (0.46)</td>
</tr>
<tr>
<td>Average thick a-Si</td>
<td>2</td>
<td>18</td>
<td>19.1 (0.80)</td>
<td>556 (8.42)</td>
<td>74 (3.9)</td>
<td>7.90 (0.59)</td>
</tr>
<tr>
<td><strong>Flat</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Best</td>
<td>1</td>
<td>1</td>
<td>12.60</td>
<td>541</td>
<td>74</td>
<td>5.01</td>
</tr>
<tr>
<td>Average thin a-Si</td>
<td>1</td>
<td>8</td>
<td>12.7 (0.16)</td>
<td>528 (13.4)</td>
<td>71 (1.79)</td>
<td>4.75 (0.24)</td>
</tr>
<tr>
<td>Average thick a-Si</td>
<td>1</td>
<td>4</td>
<td>12.4 (0.32)</td>
<td>536 (7.05)</td>
<td>72 (1.16)</td>
<td>4.79 (0.20)</td>
</tr>
</tbody>
</table>

**Figure 2.** (a) J–V curve of the nanophotonic cell, measured independently by ISE CalLab, compared to the flat one, and (b) two examples of external quantum efficiency (with symbols) and absorption spectra. The inset in (a) shows a 5 cm × 5 cm film on glass divided into 12 solar cells of 1 cm\(^2\).
merit, the light trapping efficiency (LTE), that enables comparing the optical effect of nanostructures at both short and long wavelengths, independently from the solar cell design and material. They noted that the LTE of experimental cells is significantly lower than that of theoretical structures, which can approach the Lambertian limit, LTE = 1. The present nanophotonic cell, and that of [14], present a clear improvement compared to the reported results of [37], by advancing from 0.2–0.3 to 0.56 and 0.57 respectively.

We further focus on the lowly-absorbed photons and evaluate the light-path enhancement factor of the nanophotonic cells following the same method as in [14]. The factor $F$ estimates the light-path enhancement by using a simple model of propagation of diffracted waves [38, 39]. In the long wavelength range, the absorption $A$ is given by

$$ A = \frac{\alpha d_{eq}}{\alpha d_{eq} + \frac{1}{F}}, $$

with $\alpha$ the absorption coefficient of silicon and $d_{eq}$ the equivalent thickness of the nanophotonic film (here 830 nm). The underlying assumption of weakly absorbing medium can be estimated to be valid from ~700 nm, from which less than 15% of the photons are absorbed in one pass in our layer. We obtain the best fit for the EQE of the nanophotonic cell for $F = 7.5$ (figure 3). It highlights the light-trapping effect of the self-assembled nanophotonic layer, compared to the double pass in the flat cell (absorption curves for $F = 2$, i.e. double pass with a perfect ARC and rear mirror).

It is remarkable that, in addition to the achieved enhancement, the Voc and FF of the nanophotonic cells are higher than for the flat ones. It is plausible that the front surface recombination velocity still deteriorated with the nanotexture, but the smooth profile preserved it to a sufficient level, enough to maintain the higher carrier injection induced by the higher photon collection, hence the higher Voc and FF. If optically the nanophotonic structure fully demonstrated its efficiency, we note that the Voc, although at the higher end compared to similar cells, is still below 600 mV, thus just slightly higher than the Voc of the microcrystalline silicon solar cells [40]. This implies that the nanophotonic cell does not fully benefit from the high quality of its monocrystalline material. The fitting of a 2-diode model via $Suns$–$Voc$ measurements [41] suggests that the cells do not only suffer from surface recombination, but also from recombination inside the bulk. This implies that the defects could still be introduced during the cell fabrication (most probably by the dry-etching steps [42]) or possibly already at film fabrication [43]. Thus, achieving truly competitive efficiencies is conditioned by the fabrication methods and the cell design rather than the nanophotonic light management. Techniques and designs that favor minimal material damage and excellent surface passivation with minimal parasitic absorption are the next targets, which will seemingly converge on interdigitated back-contact cells (IBC) with wet-etched inverted nanopyramids [9, 34].

In summary, the present sunlight-thin c-Si solar cell realizes the full potential of nanophotonic structures, with a doubled power-conversion efficiency. It demonstrates that with a carefully designed nanophotonic surface, light-trapping efficiency is significantly enhanced (7.5 increase of light path) while the charge-carrier collection efficiency in the absorber layer can be preserved, resulting in a solar cell with a remarkable efficiency of 8.6% on a light-wavelength-thin monocrystalline silicon substrate (830 nm equivalent thickness). The fully realized potential for these devices is expected to carry nanophotonic cells with 10–80 $\mu$m thickness in direct
competition with the current wafer-based cells of 180 μm, with efficiencies well beyond 20% [44]. In addition, the sub-micron-thin films, although not offering the winning absolute power-conversion efficiencies, provide unique flexibility and semi-transparency [45]. The latter, combined with the high stability and maturity of c-Si PV, can make them the key future players in the broad range of applications of the photovoltaic technology.

Methods

Fabricating monocrystalline thin films
The 1.1 μm thin film of monocrystalline silicon was formed via the ‘epifree’ process, based on the empty-space-in-silicon technique [46]. This lift-off method is based on the etching of regular pores inside a thick wafer, and their reorganization upon annealing, which leads to the formation of a thin defect- and void-free film floating above a single void. The pores were formed by deep-UV lithography and RIE on 200 mm wafers (p-type ~1 ohm cm), in a square pattern with 800 nm pitch, ~530 nm diameter and 3200 nm depth, for a total porosity of ~20%. The wafers were annealed at 1130 °C in 1 atm of H2 (Epsilon 2000 from ASM) [18]. The present process is of course not affordable for photovoltaics, but the possibility of forming multiple stacked films at once, and the replacement of DUV-lithography by lower-cost methods, such as nanoimprint, leave the door open for future industrial exploitation.

Processing the films into solar cells
While the film was still attached to its parent wafer, 50 nm of p+/n-type μc-SiO2:H was deposited in a radio frequency (13.56 MHz) PECVD reactor with SiH4 (13 sccm) and CO2 (1 sccm) as precursor and H2 (200 sccm) as carrier gas by adding 1.5 sccm of TMB just before a-Si:H deposition by PECVD (AK1000 from Meyer–Burger) at 200 °C. The samples were loaded in two batches with 4 months interval. Not all cells were measured, as many of the outside cells were not properly de

Nanostructuring the solar cells with amorphous order
A triple layer consisting of PDDA (polydiallyldimethylammonium), PSS (poly(sodium 4-styrenesulfonate)) and ACH (aluminum chloride hydroxide) was deposited on top of the silicon surface. Afterwards, a colloidal solution consisting of negatively charged polystyrene (PS) beads (diameter = 270 nm) was adsorbed on the surface. In a subsequent step, an etch mask was deposited on top of the PS-beads-covered substrate. Thermally evaporated aluminum (for most samples) or silicon oxide films (for one sample only) with a thickness of 50 nm were used as hard mask. The PS beads were removed by softly wiping the surface with acetone. The pattern was transferred by RIE with a SF6/O2 plasma (100 W) in a CCP reactor. The mask was removed by a short dip in dilute HF (30 s HF:HCl:H2O 1:1:20). A schematic of the process can be found in the supporting information (figure S1) and an AFM scan of the nanocup cross-section can be found in the supporting information (figure S2).

Characterizing the solar cells
For I–V measurements, the solar simulator was a Wacom class AAA (spectral match, time instability, and non-uniformity of irradiance) with a collimating angle below 5°. The cells were measured without an aperture against a reference cell which is calibrated (traceable) to the World Radiometric Reference by the European Solar Test Installation of the European Commission Joint Research Center, an ISO 17025 accredited calibration
laboratory. This reference cell was a diffused-emitter IBC cell, 4 cm². For Suns–Voc, the cells were measured in a Sinton Suns–Voc setup and the saturation current densities were taken from the software fit.

Quantum efficiency and absorption \( (A = 1 - R - T \text{ with } T = 0) \) of figures 2 and 3 were measured with a spectrophotometer on the finished cells in between two metal fingers, within a wavelength range from 300–1200 nm and integrated over the whole half space, using an integrating sphere. The spot size was 1 mm × 1 mm. The spectral step was 10 nm and the spectral width was ~2 nm. The angle-resolved absorption (figure 1(c)) was measured in a Perkin Elmer Lambda 950. The measurements were performed in an integrating sphere of 150 mm diameter with a center mount, enabling to measure \( A \) directly. The angle of incidence was varied between 10° and 40° with a step of 10°. The spot size was 2 × 5 mm² and the spectral step was 5 nm. The integrated value of absorption was calculated as follows:

\[
\phi_A = \frac{\int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} \frac{\lambda}{h c} S_{\text{AM1.5G}}(\lambda) \cdot A(\lambda) \, d\lambda}{\int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} \frac{\lambda}{h c} S_{\text{AM1.5G}}(\lambda) \, d\lambda},
\]

where \( \phi_A \) is the total number of absorbed photons and \( \phi_{\text{inc}} \) is the total incident photons (in units of number of photons/s m²), \( \lambda \) is the wavelength of light (the minimum and maximum values correspond to the wavelength range that silicon absorbs, i.e. 300–1170 nm), \( h \) is Planck’s constant, \( c \) is the velocity of light, \( S_{\text{AM1.5G}} \) is the global till solar intensity distribution at the air mass of 1.5 and \( A(\lambda) \) is the measured absorption. For the calculation of the light-path enhancement factor \( F \), the absorption coefficient \( \alpha \) was taken from Green and Keevers [47].

The nanotexture morphology was investigated by scanning-electron microscopy with secondary-electron detection, and AFM in tapping mode (Nanoscope PV, ICON-PT), with image analysis and averaging from four locations. The effective thickness was calculated assuming an ellipsoidal shape on one hand and truncated pyramids on the other, and taking the intermediate value.

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Authors contribution

AD, PRC, IG and JP supervised the work. IM and CT developed and fabricated the nanotexture, VD designed, fabricated and characterized the solar cells. WC developed and deposited the \( \mu \)c-SiO\(_x\) layers and measured the angle-resolved absorption. All co-authors contributed to the discussion. VD wrote the manuscript with help from the co-authors.

The authors declare no competing financial interests.

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