Self-Contained Optical Enhancement Film for Printed Photovoltaics

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Abstract

Printed photovoltaics promise lightweight and flexible light harvesting devices for conformal integration into buildings, portable electronics or vehicles. This is enabled by employing thin photoactive layers, which can reduce the use of sometimes costly and scarce absorber materials. Since this in turn comes along with an incomplete light absorption and hence restrains the power conversion efficiency of printed photovoltaics, their development was since long accompanied by integrated light management. However, besides a mere efficiency enhancement, new strategies should consider both functionality and additional costs of the light management. Optical enhancement strategies should consequently avoid complications with the delicate printing of the photovoltaic layers and therefore structures on the light incident surface of the device have been proposed. However, these air-faced approaches are prone to the impacts and stress of operating conditions and hence a protected solution is desired. Here we introduce a carefully designed photonic nanostructure embedded in a self-contained transparent film, which offers a conformal device attachment. An efficiency enhancement of 11% is demonstrated on an organic photovoltaic device. Angle dependent measurements moreover suggest a yearly increase of 13%, exploiting the seasonal asymmetry of the incident solar power by a built-in asymmetric

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diffraction.

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1. Introduction

Certified record efficiencies for printable photovoltaic technologies are ranging between 22-23% for CIGS, CdTe and perovskite solar cells [1, 2, 3] and between 10-13% for CZTS, dye-sensitized and organic solar cells. [4, 5, 6, 7]

5 The continuous improvements during the past years were enabled on the one hand through material and process development [8, 9, 10] and on the other hand by a wide variety of optical enhancement schemes. [11, 12, 13] Existing solutions have thereby often been introduced as scattering or diffractive structures in the vicinity of or even directly in the active layer, in order to obtain

10 coupling into guided modes. [14, 15, 16] If metallic layers are involved, surface plasmon polaritons can additionally be excited which in turn can give rise to strong confined fields in the absorber layer. [17, 18, 19] However, light management strategies should ideally neither compromise the electronic properties of the solar cell [20, 21] nor add costs or complications to the large-area fab-

15 rication of the photovoltaic devices. [12, 14, 22] Whereas the implementation of structures inside the functional photovoltaic layers could hinder appropriate morphology and phase formation, increase interface recombination or introduce additional parasitic absorption in the device, light management structures located on the surface provide an excellent alternative solution. Absorption

20 enhancements through light redirection and antireflection strategies have been reported [23, 24, 25, 26, 27, 28, 29, 30, 31, 32], which successfully avoid manipulation of the printed functional layers. However, these structures have their functional optical interface exposed to air and hence cannot sustain typically outdoor conditions of printed photovoltaic operation without losses in their op-

25 tical properties. Up to now, only a single approach provided a protected surface structure that is designed with an unstructured air interface, but with efficiency

enhancement only below 7%. [33]

Here we propose a self-standing and non-absorbent light management film with an unstructured sunward surface, which can be independently attached
30 to the substrate of thin film photovoltaics. The film consists of a carefully designed high refractive index periodic nanostructure of large aspect-ratio, which is embedded in a polymer matrix to protect it from external influences and contamination. By introducing an optimized asymmetric shape, a large portion of the light is diffracted into the first order [34] and is further trapped in the device.
35 The structure generates a 11% enhancement in the power conversion efficiency (PCE) of an organic photovoltaic device printed in ambient atmosphere.

2. Optical simulations

The commercial software SETFOS (Fluxim AG, Switzerland) was used to calculate the optical properties of the solar cell. The absorption in the active
40 layer is determined dependent on the propagation angle in the substrate θ_S , which is the angle accessible through light redirection structures. Secondly, for each geometry of the ZnS nanostructure (see Fig. S1), the diffraction efficiencies η_m and the resulting propagation angles up to the fourth order $m = \pm 4$ were calculated for both polarizations using rigorous coupled wave analysis (RCWA).
45 [35] Through the initial diffraction event, a set of possible light propagation angles $\theta_S(m)$ is defined for every wavelength λ . The above calculation is hence repeated for incidence angles $\theta_S(m)$ for both directions of incidence (top and bottom) and the results are stored in bidirectional scattering distribution functions BSDF(λ) with dimension equal to the number of propagating diffraction
50 orders. Once the coherent optics of the solar cell stack and the nanostructure layer are calculated, they can be treated as interfaces [36] with angle dependent reflection, transmission or absorption coefficients. As described in [37, 38] the BSDF and the results from SETFOS are then used to calculate the optics of the incoherently coupled system, connected only through transparent thick layers
55 (glass/polymer). From the resulting absorption in the active layer, the current

Figure 1: Fabrication of the light-management layer onto a solar cell substrate. (a) An UV-curable polymer is dispensed onto a large area and molded by a structured master. (b) After UV curing, a high-index zinc sulfide (ZnS) layer is obliquely evaporated onto the hardened structure. Through self-shadowing of the grating pillars an asymmetric layer is formed. (c)-(d) A second layer of the polymer is then applied and cured to embed the ZnS nanostructure. (e) The resulting diffractive film is attached to the substrate for printing of the photovoltaic layers. (f) SEM picture taken of the cross section of the high-index nanostructure layer.

density can be evaluated for various incident angles.

3. Experimental

3.1. Device Fabrication

In order to be compatible with large-area production, interference lithog-
60 raphy [39] is used to create the designed nanostructure with period Λ from
which a nickel master is created. This template further enables cost-effective
and large-ares continuous nanoimprint lithography [40, 41] through either hot
embossing into flexible substrates or UV-lithography of a sol-gel [42, 14]. Fig.
1(a)-(d) show how the latter is used here to imprint an UV-curable polymer
65 (micro resist technology, OrmoStamp), which is dispensed over the full light
incident side of the solar cell substrate. Once it is hardened on the area of 25
cm² by UV light and successively baked it exhibits a high mechanical (hardness
of 36 MPa, Young's modulus of 0.65 GPa) and thermal (up to 270°C) stabil-
ity and is further highly transparent for UV and visible light [43, 44]. Tilted
70 evaporation (45°) of the transparent and high index-of-refraction material zinc
sulfide (ZnS) is used to obtain a periodically modulated asymmetric optical in-

interface through self-shadowing of the previously molded pattern.[34] Once the
 structure is embedded with another layer of the UV-polymer it forms a self-
 contained diffractive film, which is attached to the photovoltaic substrate. A
 SEM image of the final nanostructure is shown in Fig. 1(f) (Fig. S1) and re-
 reveals the ZnS coated side faces. Polymer solutions with standard architecture of
 ITO(150nm)/Clevios P-VP AI4083(30nm)/Merck Lisicon PV-D4610:PC₆₀BM
 [1:2](130nm)/Ca(30nm)/Al(100nm) were doctor-bladed in ambient atmosphere
 (Fig. 1) as described previously. [45] The standard device architecture and
 small device area is used to test the light management on an increased number
 of reference devices. Since the light management film is decoupled from the de-
 vice and independent on its fabrication, no tests on durability or up-scaling of
 the organic solar cells are performed and can be found elsewhere. [46, 47, 48, 49]

3.2. Sample characterization

J-V curves were recorded under illumination of 1 sun, provided by the xenon
 arc lamp of a solar simulator (sciencetech SS2.5kW) equipped with an AM1.5
 filter and a collimation of ± 3 degrees. A power density of 100 mW cm^{-2} was
 ensured using a calibrated Si-photodiode (VLSI Standards). The samples were
 masked with an aperture of $A = 0.04 \text{ cm}^2$, mounted in a N₂-filled housing and
 illuminated through a quartz window. A Keithley 2400 source meter was used
 to ramp the voltage from -1.3 V to 1.3 V in steps of 0.01 V with a dwell time
 of 60 seconds to avoid heating of the device. The obtained current densities
 were multiplied with a correction factor accounting for the spectral mismatch
 and the Fresnel reflection at the quartz window ($n \approx 1.5$). Additional data
 on statistical variations and error analysis can be found in Fig. S2. For angle
 dependent measurements a constant distance to the light source was ensured for
 all angles of incidence. External quantum efficiency (EQE) was measured in a
 N₂-filled glovebox using the light of a xenon lamp passing through a monochro-
 mator and guided to the masked ($A = 0.04 \text{ cm}^2$) sample through an optical
 fiber. Currents obtained from integration of the EQE-curves were compared to
 the values obtained from J-V measurements (see Fig. S3) yielding deviations

below 6%.

The diffraction efficiency of the nanostructure was measured with a semi-
105 cylindrical glass lens attached on the backside of the sample to preserve the
diffraction angle. Collimated white light was incident on the structure and in-
tensity spectra were recorded behind the sample in steps of 2 degrees.

4. Results and discussion

110 4.1. Design of the Nanostructure

Compared to previously proposed air-faced light management, an embedded
diffractive nanostructure is not only protected against environmental influences
but provides beneficial additional optical properties. As known from previous re-
ports, an oblique light propagation can enable a more preferred electromagnetic
115 field distribution throughout the photoactive layer and in consequence an in-
creased absorption [50, 51, 52] For a periodic nanostructure this can be achieved
by transmitted light of non-zero diffraction orders $T_{\pm 1, \pm 2, \dots}$, [45] which propa-
gate at angles $\theta_S(\lambda)$ in the substrate (see Fig. 2a). Whereas $\theta_S(\lambda)$ is dependent
on the period Λ , the amount of light coupled to a diffraction order at a certain
120 wavelength can be controlled by the material and shape of the nanostructure
(see Fig. S1) and can hence be widely adapted to a given device type. A second
unique property arises from the embedment of the nanostructure (Fig. 1d) in
combination with an introduced asymmetry. In contrast to periodic structures
exposed to air, diffracted light cannot easily escape the device after reflection
125 from the solar cell. For wavelengths $\Lambda \leq \lambda < n\Lambda$ the propagation angle of light
of the first diffraction order exceeds the critical angle for total internal reflection
(TIR) at the polymer-air interface θ_{TIR} and hence the light is largely hindered
from escaping the device. Instead it is redirected back onto the diffractive layer
and the PV stack as long as it leaves the device through a successive diffraction

130 event ([A] or [B] in Fig. 2a).

Fig. 2b shows the summed transmission efficiency $\eta_{\pm 1}^T$ of the positive and negative first diffraction order for three nanostructure geometries. Starting with an ZnS coating that symmetrically follows a sines profile, we obtain a total
 135 efficiency of up to 70% equally split into both orders. In this case, however, due to reciprocity the light will escape the device upon incidence on the grating from below ([A]) as efficient as it is couples to the initial diffraction order (blue curve in Fig. 2c). Introducing an asymmetry into the coating gives rise to two effects: on the one hand the light is diffracted more efficient into the T_{+1} order
 140 than into T_{-1} and on the other hand the loss of this light is suppressed at the second diffraction event. The efficiency of this loss is indicated by the red line in Fig. 2(c) and corresponds to the light that after diffraction into T_{+1} is reflected from the solar cell and escapes via diffraction at the nanostructure from below ([A] in Fig. 2a). It gets apparent, that for straight incidence this equals the
 145 inverse process for initial light, which is coupled into the weak T_{-1} order (Fig. 2b, middle).

This asymmetry of η_{+1}^T and η_{-1}^T can be further enhanced by optimizing the shape of the nanostructure. This is achieved by changing the underlying periodic structure, indicated in Fig. 2b (bottom) or the ZnS coating parameters
 150 (see Fig. S1). Through additional variation of period and depth, the nanostructure is optimized to yield the highest current density in the present solar cell. The fabricated structure slightly deviates from the theoretical maximum and is indicated by the blue cross in Fig. 2d (see also Table S1). Fig. 2b shows the measured T_{+1} diffraction efficiency, which reveals a maximum of $\eta_{+1}^T = 75\%$
 155 and an average of $\eta_{+1}^T \approx 60\%$ between $450 \text{ nm} < \lambda < 750 \text{ nm}$ in good agreement with the simulation. Despite the total amount of light in $T_{\pm 1}$ is increased with respect to both sines shapes, at the same time the efficiency η_{-1}^T is further reduced, which also reduces the loss through escape path [A] below 5%. For a third diffraction event the portion of the light diffracted towards the surface ([B]
 160 in Fig. 2a and 2c) remains below 3% for $450 \text{ nm} < \lambda < 800 \text{ nm}$ for all three

Figure 2: Design of the photonic nanostructure. (a) Sketch of the light path in the device with an embedded diffractive film. For $\Lambda \leq \lambda < n\Lambda$ the transmitted light of the first diffraction order T_{+1} propagates with angle $\theta_S(\lambda) > \theta_{TIR}$ in the substrate and undergoes total internal reflection at the polymer-air interface (b) The sum of positive and negative first transmission orders and their ratio is strongly influenced by the shape of the nanostructure. (c) In contrast to symmetric shapes, the successive escape channels (A and B) can be suppressed with an asymmetric coating. (d) Dependent on period and depth of the nanostructure the structure can be optimized for highest current generation in the solar cell. The white cross marks the maximum, while the light blue cross indicates the structure fabricated in this work.

geometries.

4.2. Absorption enhancement

Fig. 3a shows the electronic characterization of the fabricated devices with and without the light management. An average 10% increase in the short circuit current density J_{SC} of devices with the light management film is obtained with respect to the reference devices. Since the structure does not interfere with the photoactive layer formation, we note that other electrical properties of the device remain unchanged (see Table 1). This leads to a direct translation of the enhancement onto the PCE of the device. The J-V curves of the best solar cells of each set are shown in Fig. 3b, which yield a representative 10.7% increase in PCE, close to the average efficiency enhancement of 10.5%. It has

Figure 3: Photovoltaic device characterization. (a) Enhanced absorption through the light management film yields an increased short circuit current density J_{SC} compared to the same device on an untreated substrate. (b) The JV-characteristics of the best device of each set reveal that the improvement in the current is directly converted into an enhanced overall output power of the device. (c) External quantum efficiency (EQE) of the solar cells with and without the attached light management layer. The vertical line indicates the nanostructure period $\Lambda = 535 \text{ nm}$. (d) Resulting averaged EQE enhancement ratio is in good agreement with the simulated absorption enhancement in the active layer.

to be emphasized that since our embedded light management film exhibits a unstructured sunward surface for functional reasons, no anti-reflection effect is provided by the embedded nanostructure. Simulations of the same material
175 composition without patterning revealed an even higher reflectance compared to bare glass, which rules out the influence of reduced specular reflections due to additionally introduced surface layers (see Fig. S4), but emphasized the importance of the nanostructure design. However, as for any other flat (glass) surface, anti-reflection structures can be applied additionally or even imprinted
180 in the outer cladding of the light management film (Fig. 1c-1d), which can give rise to an absorption increase of around 4% [24].

Fig. 3c shows the EQE for all devices with (orange) and without (blue) the light management layer. The average of the two sets is displayed as black line on top of the curves. A distinct enhancement in EQE is observed for $\lambda \geq \Lambda$,
185 where the diffraction efficiency reaches a maximum and the diffraction angles exceed θ_{TIR} at the surface, which both leads to a more efficient light absorption. The ratio of the two black curves is shown as red line in Fig. 3d. It reveals a broadband enhancement starting at around 500 nm and exhibiting a maximum (+85%) close to the band-edge of the photoactive layer at 720 nm, which is

Table 1: Photovoltaic parameters under AM1.5G illumination (100 mW cm^{-2}).

Substrate	V_{OC} [mV]	FF [%]	J_{SC} (max) [mA cm $^{-2}$]	PCE (max) [%]
Reference	720 ± 10^a	76.4 ± 1.7	9.9 ± 0.5 (10.57)	5.46 ± 0.25 (5.70) b
with optical film	730 ± 10	75.8 ± 2.3	10.8 ± 0.46 (11.37)	6.03 ± 0.43 (6.31) b
Enhancement			$\uparrow 9.8\%$ ($\uparrow 7.5\%$)	$\uparrow 10.5\%$ ($\uparrow 10.7\%$)

a) The stated error is the sum of the standard deviation σ of the sets of 19 and 16 samples for reference and nanostructured substrate, respectively and the systematic error, which is estimated as σ of multiple measurements of the same cell; b) Shown in Fig. 1h

190 in good agreement with the prediction of our optical model (grey curve) even though the measured enhancement is a little lower for $\lambda > \Lambda$.

Using the optical model, it is possible to reveal the two enhancement mechanisms of the embedded nanostructure. If only the first diffraction and absorption
195 event is taken into account and all reflected light is neglected, the dotted green curve in Fig. 3d is obtained. This situation is comparable to symmetric air-faced nanostructures. It matches the experimental data well in regions where the materials absorption is strong ($580 < \lambda < 680 \text{ nm}$), but it is not sufficient to reproduce the enhancement for larger wavelengths. If the successive diffraction
200 events, however, are taken into account, the predicted enhancement increases and shifts towards the band-edge of the absorber (+130% at 710 nm), representing the light trapped in the device. It thereby contributes to the absorption as long as it travels within the geometric extend of the charge collecting electrode area. The shape of the electrode was not considered in our model and may be
205 the reason for the overestimation of the simulated enhancement in Fig. 3d.

5. Performance during a solar year

5.1. Simulations

With the parameters of the fabricated nanostructure (Table S1) the absorption in the active layer $Abs(\lambda, \theta)$ is simulated for two planes of incidence, which are spanned by the wavevector of the incident light and the surface normal and which can be either parallel (azimuthal angle $\phi = 0^\circ$) or perpendicular ($\phi = 90^\circ$) to the grating vector G (see Fig. 4). Additionally, for the asymmetric direction positive and negative angles have to be distinguished. For a given location (Latitude 47.565436, Longitude 7.602925) the Bird Simple Spectral Model (SPCTRAL2.xls), provided online by the U.S. Department of Energy (DOE)/NREL/ALLIANCE, was used to access the zenith angle, azimuth angle, spectrum and power density for every hour of the year. Since simulations were only done for $\phi = 0^\circ, 90^\circ$, absorption of intermediate azimuthal angles $0^\circ < \phi < 90^\circ$ was approximated to be linearly related to the extreme values and the current density is calculated by

$$J_{sc} = \frac{e}{hc} \int_{\lambda} \eta_{IQE} \cdot [k(\phi) \cdot Abs_{\phi=90^\circ}(\lambda, \theta) + (1 - k(\phi)) \cdot Abs_{\phi=0^\circ}(\lambda, \theta)] \cdot S_{\phi, \theta}(\lambda) \lambda d\lambda, \quad (1)$$

with $k(\phi) = |\phi/90^\circ|$ for $\phi \leq 90^\circ$; $k(\phi) = |(\phi - 180^\circ)/90^\circ|$ for $\phi > 90^\circ$ and η_{IQE} set to 0.9. Here, e is the elementary charge, h is Plank's constant and c is the vacuum speed of light.

5.2. Angle dependent measurements

In order to access the impact of the light management for realistic operation conditions, angle dependent J-V measurements were performed in steps of 5 degrees. Fig. 4(a) shows the measured J_{SC} for incident angles in the parallel case and in the perpendicular direction and the PCE at various angles of incidence is shown in Fig. 4(b). Along both directions the PCE enhancement through the light management can be kept over $\Delta\theta_{\phi=90^\circ} = \pm 40^\circ$ and $\Delta\theta_{\phi=0^\circ} = \pm 30^\circ$, respectively. Since independent on the location the angular span between summer

Figure 4: Yearly light harvesting with the light-managment. (a) Angle dependent short circuit current J_{SC} of the device with the light management film, measured for two azimuth angles ϕ with respect to the grating vector G and compared with the respective simulations. (b) Angle dependent efficiency for the two directions under simulated 1 sun illumination, compared to the reference device (shaded). (c) Sketch of the seasonal and daylight angles of incidence of the sun and (d) the corresponding solar power density of the respective position of the sun throughout the year calculated for Basel, Switzerland. (e) If the device with the light management is tilted by the latitude angle β , the angular span (red/blue cross) in which the conversion efficiency with the light management is superior to the reference covers the times of most powerful solar radiation.

and winter equals twice the equator's tilt with respect to the ecliptic ($\pm 23.4^\circ$), this enhancement is already sufficient to improve the performance for all seasons if oriented properly (see Fig. 4c) but a little too small for covering the whole daylight movement ($\pm 90^\circ$).

5.3. Yearly harvesting

However, in terms of delivered power the sun's seasonal movement apparently exhibits a certain asymmetry. For locations outside the tropical zone, the proximity of the sun and hence the delivered power has its maximum in summer and decreases steadily towards winter as shown in Fig. 4d. In contrast, the

daylight movement has its power maximum around noon and is symmetric with respect to morning or evening. Hence, a light management structure which exhibits an enhancement for a small range of angles $\theta_{\phi=0^\circ} \leq 25^\circ$ with high asymmetry but an enhancement for a preferably wide range of angles $\theta_{\phi=90^\circ}$ in the perpendicular direction with symmetric behavior is perfectly suited to maximize the energy harvested during a solar year. If we position our device facing south with a tilt equal to the local latitude β as shown in Fig. 4e, we can cover the whole zenith angle distribution with our enhancement range ($\phi = 0^\circ$, blue bar) and most of the azimuthal distribution range ($\phi = 90^\circ$, red bar). Assuming clear sky conditions, an average fill factor of 70% and a constant V_{OC} of 700 mV, the energy harvested by the photovoltaic device without light management in this conditions can be approximated to be $77.0 \text{ kWh m}^{-2} \text{ year}^{-1}$. With the attached light management film, however, a generated energy of $87.4 \text{ kWh m}^{-2} \text{ year}^{-1}$ (+13.4%) is obtained, increasing the yearly power conversion efficiency of the device in this configuration from 6.6% to 7.5%.

6. Conclusion

In summary we presented an embedded light management film with an unstructured surface, which makes it durable and resistant to environmental and mechanical influences during photovoltaic operation. The self-contained film can be fabricated independent of the device by a mass-production compatible method and provides a perfect platform for future wavelength dependent optical engineering of preferable interference conditions in various thin film photovoltaic systems. In contrast to air-faced structures additionally light trapping yields up to 85 % EQE increase near the band edge of the photoactive layer. The asymmetric structure leads to a highly efficient diffraction and secondly exhibits an angular performance dependence, which matches the distribution of incident solar power through the year. An overall enhancement at simulated standard test conditions of 11% is obtained and the yearly harvested energy was predicted to be increased by more than 13%. Although the presented structure was op-

timized for straight incidence (tilted installation), any other angular response
is accessible through variations of the shape and structural parameters of the
high-index nanostructure.

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Appendix A. Supplementary Material

Supplementary data associated with this article can be found online.

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