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Superhard antireflective textures based on hyperbranched polymer composite hybrids for thin film solar cells encapsulation

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Abstract

In this study, we demonstrate by simulation and experiment the antireflective (AR) performance of hyperbranched polymer (HBP) nanocomposites textures replicated from a moth-eye pattern using UV nanoimprint lithography. A UV-curable acrylated HBP and a hybrid composite of the HBP with silica nanoparticles and an organometal precursor were used. Using effective medium theory (EMT) simulations, optimal patterns were found to be arrays of paraboloids with stable AR performance over a large range of geometries. A good agreement was found between the simulated and measured optical behavior of such AR arrays with a normal reflectance within the visible range of around 4% when using a glass substrate. The photocurrent of AR coated a-Si:H solar cells was found to be 2% higher than the reference value of an uncoated cell whereas for AR coated tandem thin film Si cells the increase was 3% for the top a-Si:H cell and 2% for the bottom microcrystalline Si cell.

Antireflective hardcoats: Synthetic moth eye textures eliminate light reflection in the front encapsulation of solar cells, leading to a 5% photocurrent increase in thin film tandem a-Si:H and μ c-Si devices. The sub-micron antireflective textures are optimized using optical simulations and replicated in a low shrinkage and superhard hyperbranched polymer nanocomposite hybrid by means of a UV nanoimprint lithography process.

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Keywords: antireflective textures, hybrid nanocomposites, imprinting, nanostructures, thin film silicon solar cells

Introduction

The reflection of solar light in the front encapsulation of a solar cell results in a decrease in collecting efficiency of the device.^[1] For a flat interface between air and a material such as glass and polymers with an index of refraction (n) of 1.5, the hemispherical reflectance is around 15%, and only 85% of the

incoming light is transmitted into the cell.^[2] Conventional strategies to minimize reflection losses are based on multilayer interferential film structures.^[3] An alternative is in the form of texturized coatings with a gradient in n , from 1 (air) to 1.5 (polymer or glass).^[4] Well-known examples found in nature include the eyes of moths^[5] or insect wings,^[6] which are antireflective to visible light due to a gradual transition of the index n from air to the material.^[7] Such structures eliminate steps in the index n at interfaces between layers and suppress Fresnel reflection.^[2, 8] The texturized coating approach was found to be effective to encapsulate solar cells, leading to a total gain in photocurrent of around 5 % in the case of polymer textures on the air/glass surface of “micromorph” thin film silicon solar cells.^[9] Antireflective (AR) texturized surfaces are patterns of subwavelength nanoscopic pillars, each approximately 200 nm in diameter and height,^[10] acting altogether as an effective medium with axial gradient in n . The cross-section geometry of the structures defines the profile of the n gradient^[11] as detailed in a number of theoretical studies.^[12] The optical behavior of AR patterns is controlled by the height, the period and the cross-section geometry of the AR features. When the period of the structure is sub-wavelength, effective medium theory (EMT) can be used to simulate the interaction of light with the periodic nanostructure. EMT assumes a film stack where each layer corresponds to a distinct level of the surface-relief profile.^[13] In this way, the influence of the variations on the aspect ratio of the features can be studied and optimal parameters can be found. For an ideal AR surface, the period of the features should be as fine as possible (unresolvable by light) and its height as large as possible (for a large enough gradient of n).^[4b, 7] The production of AR textures has been demonstrated for a variety of materials such as Si or polymers.^[14] Texturized polymer surfaces have been replicated using nanofabrication methods,^[15] primarily through ‘top-down’ approaches evolving from microfabrication^[16] such as nanoimprint lithography (NIL)^[17] and UVNIL.^[18] The potential of these patterning methods for the cost-effective production of functional surfaces over large areas is claimed to be very high thanks to the development of roll-to-roll (R2R) processing.^[19] However, several hurdles currently limit such a potential, due to e.g. dynamic wetting instabilities and lack of replication fidelity due to polymerization shrinkage.^[20] Indeed, whereas high aspect ratio nanostructures lead to better AR performance,^[21] such features may be difficult to replicate into polymers. Moderate aspect ratio nanostructures have already been successfully transferred into various polymers with satisfactory results.^[14b, 22] In particular, hybrid silica-hyperbranched polymer (HBP) nanocomposites enabled sub-micron sized structures to be replicated under low pressure with very high fidelity owing to their low viscosity and low shrinkage, using an optimal dual-cure process sequence.^[23] Such hybrid materials would represent low shrinkage alternatives to commercial photoresists, and would moreover provide anti-scratch surfaces owing to their superior hardness.^[23] The objective of the present work was to produce AR textures based on both soft HBP and hard HBP composites and evaluate their optical behavior and influence on the photovoltaic performance of thin film silicon solar cells. Attention was also paid to simulate the influence of the periodic texture geometry, including the degree of replication fidelity, on its AR behavior.

Results and Discussion

Optical simulations

This section describes the influence of the size of cones and paraboloids on the reflectance of sub-micron hexagonal arrays using optical simulations. Figures 1 and 2 depict the simulated total reflectance (R) of cones and paraboloids with a base diameter of 300 nm and various heights, compared with a flat surface of a $n = 1.5$ material (glass or HBP), for which $R = 4.3$ %. All simulated textures exhibit a lower R compared with the flat surface, a result of the effective optical gradient. One also notices that the overall behavior of both textures is quite similar, with a faster decay at low wavelengths for paraboloids. A decrease in reflectance is moreover evident with increasing feature size, to values as low as 0.12 % at wavelength around 500-600 nm for 300 nm height cones and 0.21 % for 300 nm paraboloids. In the case of 600 nm height features, values of 0.05 % for cones and 0.1 % for paraboloids are reached. These results are in accordance with literature, where better AR properties were reported for cone shaped features.^[11b-d]

Fig. 1: Simulated reflectance vs. wavelength for periodic arrays of 300 nm base diameter cones with different heights h_0 .

Fig. 2: Simulated reflectance vs. wavelength for periodic arrays of 300 nm base diameter paraboloids with different heights h_0 .

Figure 3 shows the simulated average reflectance between 380 and 780 nm versus feature height for cones and paraboloids. An average reflectance of 0.3 % is obtained for cones higher than 240 nm and paraboloids higher than 190 nm. It is also evident that cones are more sensitive to height changes in the range 200-300 nm than paraboloids and their AR performance is thus more sensitive to polymerization shrinkage and resulting reduction of feature height upon replication. Considering the 300 nm deep master structure, even a shrinkage of 33 % (equivalent to a loss of 100 nm in height), paraboloids keep the same reflectance performance. As a consequence, paraboloids should be preferred for UVNIL production of AR surfaces.

Fig. 3: Average reflectance vs. feature height for periodic arrays of 300 nm base diameter cones and paraboloids.

Replication of antireflective textures

In the previous section, we showed that paraboloid arrays exhibit excellent antireflective properties in the visible range. This section examines the optical behavior of a replicated polymer based moth-eye surface texture on a glass substrate. The hexagonal moth-eye array of the Ni template is shown in Figure 4. It is characterized by a period equal to 350 nm, identical along the three main directions of the pattern. The nanoscale roughness revealed by the high resolution microscopy technique resulted from the electroforming fabrication process [24].

The HBP and hybrid textures replicated from the nickel template are also shown in Figure 4. The quality of the replication was excellent for both materials, which accurately reproduced the nanoscale roughness of the template. However, the period of the HBP replica along the main axes was lower than that of the template and equal to 341 nm. The corresponding 2.6 % in-plane contraction was a consequence of polymerization shrinkage, which actually manifested itself upon release from the glass carrier. Assuming material isotropy, the shrinkage along the vertical dimension would be 1.3 %, which is extremely small.

For the hybrid replica the period was also lower than that of the template and equal to 335 nm. The corresponding 4.5 % in-plane contraction was higher than that of the HBP and was considered to result from the condensation process, in addition to the polymerization shrinkage during the dual-cure process. [20a] The shrinkage along the vertical dimension would be 2.3 %, again assuming material isotropy. The present very high replication fidelity for the hybrid material was achieved thanks to an optimal sequence for the dual-cure process, with UVNIL carried out 45 minutes after the condensation reaction had started. This precise timing was key, in order to benefit from the low viscosity for processing and minimize shrinkage stress. [23]

In fact, according to the data shown in Figure 3, the very low shrinkage of both HBP and hybrid materials should have no detectable influence of the reflectance of the texturized surfaces.

Fig. 4: High-resolution electron micrographs of the nickel master (a, b and c), HBP replicates (d, e and f) and hybrid composite replicates (g, h and i).

The total reflectance and transmittance behavior of the polymer materials are presented in Figures 5 and 6, respectively, and compared with the simulated behavior of an hexagonal array of 300 nm high paraboloids. The flat HBP and hybrid materials behave similarly to glass with a reflectance of around 8 %, within the 0.5 % experimental accuracy (4 % corresponding to the front surface reflection and 4 % from the rear surface reflection). However, after imprinting the polymer materials with the moth-eye pattern on the top of the glass support, a reduction in reflectance from 8 % to 4 % was obtained. The remaining reflectance of 4 % corresponded to the back surface of the glass support. A good agreement between simulation and experimental measurements is moreover evident, with a difference within the experimental accuracy of 0.5 %. The antireflective polymer texture thus almost totally eliminated the reflection of the top surface of the glass.

Fig. 5: Total reflectance for glass, HBP and hybrid materials and texturized HBP and hybrid coatings on glass.

These results were confirmed by the transmittance measurements, with a value of around 92 % for the 1 mm thick bare glass and the 100 μm thick flat HBP and hybrid materials. The significant drop of transmittance for the latter materials at wavelengths below 500 nm resulted to some extent from the light absorption of the photoinitiator in the range from 300 to 400 nm. The difference between the two materials also reflected the different concentrations of photoinitiator (6 wt% in the HBP and 4.8 wt% in the hybrid).

The transmittance of glass with texturized coatings was clearly improved compared with uncoated glass and comparable for both HBP and hybrid materials. It was close to 96%, except for wavelengths below 500 nm where the transmittance linearly decreased. This peculiar behavior had already been observed by other authors^[4b, 25] and was attributed to the degradation of the transmitted wavefront by light scattering within periodic nanostructures. For transparent patterns one expects a transmittance enhancement for wavelengths below $2.5 h_0$ and above np at a normal incidence,^[4b, 7] that is, below approximately 750 nm and above 500 nm in the present case. By reducing the period of the nanostructured pattern, the enhanced transmittance window can be moved to lower wavelengths.^[25a]

Fig. 6: Total transmittance for glass, HBP and hybrid materials and texturized HBP and hybrid coatings on glass.

The simulated transmittance did not drop at wavelengths below 500 nm, as no light scattering structure was present in the simulated multilayer stack and no photoinitiator absorption was considered either.

Solar cells

The polymer-based textures were deposited at the air-glass interface of two types of thin film silicon solar cells. Figure 7 shows the external quantum efficiency for normal incidence of a-Si:H solar cells with and without texturized coatings. A very similar behavior was obtained for both HBP and hybrid textures, with a gain in photocurrent of approximately 2 % compared with the reference cell without the AR textures (Table 1).

Fig. 7: External quantum efficiency of a-Si:H solar cells with and without antireflective HBP and hybrid coatings.

Figure 8 shows the improvement in external quantum efficiency for micromorph tandem cells obtained at a normal incidence with the HBP and hybrid AR coatings. Photocurrent gains of 3.5 % and 1.8 % were measured for the top a-Si:H and bottom μ c-Si cells, respectively. This difference in performance between top and bottom cells was due to the particular feature height used for the AR texturization. As shown in Figure 2, the minimum in reflectance shifts to higher wavelengths with increasing feature height. As a consequence, 300 nm height paraboloids are less antireflective beyond 800 nm, where μ c-Si is more absorbing. Therefore, to maximize AR properties for μ c-Si solar cells, higher aspect ratio features should be used.

Fig. 8: External quantum efficiency of a-Si:H and μ c-Si tandem solar cells with and without antireflective HBP and hybrid coatings.

Table 1: Short circuit current J_{sc} of a-Si:H and tandem solar cells with and without antireflective HBP and hybrid coatings.

AR coating	a-Si:H cell		Tandem cell			
	J_{sc} [mA cm ⁻²]	Current gain [%]	J_{sc} top cell [mA cm ⁻²]	Current gain [%]	J_{sc} bottom cell [mA cm ⁻²]	Current gain [%]
None	16.29	–	12.97	–	11.54	–
HBP	16.63	2.1	13.44	3.6	11.76	1.9
Hybrid	16.61	2.0	13.42	3.5	11.74	1.7

In this work, the experimental measurements were limited to a normal light incidence, when more light reflection is expected at lower incidences. The optical behavior of the AR coatings at different incidences was thus predicted using TFCalc simulations. Figure 9 shows the reflectance of glass at different incidences (cone's half-angles) with and without an AR coating on the top surface, and for both front and flat rear glass interfaces. The present simulation with equal intensity distribution for all angles of incidence yielded a reflectance value of around 15 % for a flat air-polymer interface and a cone angle of 170°. When using a paraboloid shape graded n from air to polymer, this hemispherical reflectance is reduced to around 6 %.

Fig. 9: Simulated reflectance at different incidences (cone's half-angle) for glass with and without AR coatings on the front interface.

To summarize, paraboloid HBP and hybrid textures yielded the same AR performance owing to their low shrinkage and high replication fidelity. In addition, the hybrid nanocomposites are harder and are more thermo-mechanically stable than the HBP, and thus represent interesting candidates for durable AR coatings. The hybrid approach is indeed versatile and enables to produce a broad composition range with low viscosities, suited for low pressure replication processes,^[23] which was confirmed by the present investigation. The present printing technology and hybrid formulation are both compatible with cost-effective roll-to-roll processes, i.e., with good potential to increase the efficiency of solar cells at a very low cost.^[19b]

Conclusions

The aim of this work was to develop and test a nanotexturized polymer composite coating to suppress light reflection and enhance light transmission on the front encapsulation of solar cells. Antireflective textures based on a periodic moth-eye nanostructure were replicated into HBP and hybrid nanocomposites using a UVNIL process. The hybrid was 71 % harder than the HBP and its viscosity was in the Pa.s range. EMT simulations were carried out to optimize the texture geometry and understand the possible impact of polymerization shrinkage on replication fidelity and AR performance of the texture. The simulated reflectance of periodic arrays of sub-micron cones and paraboloids was found to be similar, with minimum reflectances as low as 0.1-0.2 % for 300 nm height features. The reflectance R of surfaces with cones was found to be very sensitive to the aspect ratio of the cones for heights in the range 200-300 nm, in contrast to paraboloids for which R was almost constant in that range. The simulated reflectance of paraboloids was found to be very close to the moth-eye HBP and hybrid replicas. These texturized coatings were effective to increase the transmittance of glass in the visible range owing to a reduction of reflectance from 8 % to 4 %, and in spite of losses at wavelengths below 500 nm due to photoinitiator absorption and light scattering. The photocurrent of AR coated a-Si:H solar cells was found to be 2% higher than the reference value of an uncoated cell while for tandem solar cells the increase was 3% for the top a-Si:H cell and 2% for the bottom μ c-Si cell, as a result of the higher amount of light reaching the solar cells. The simulated reflectance for all angles of incidence predicted excellent omnidirectional AR behavior for these coatings with an hemispherical reflectance as low as 6 %.

Experimental Section

Materials and processing

The HBP was a polyester acrylate oligomer with a functionality of 16, a density of 1.13 g cm^{-3} and a newtonian viscosity of 0.2 Pa.s (CN2302, Sartomer). The properties of the HBP are reported in Table

2. The photo-initiator was 2,4,6-trimethylbenzoyldiphenyl phosphine oxide (Esacure TPO, Lamberti) at a concentration of 6 wt%. Hybrid HBP nanocomposites with 20 vol% of silica were synthesized using silica nanoparticles and organometal precursors by combining mixing and sol-gel processes as detailed in [23]. The nanoparticles were methacrylated amorphous fumed SiO₂ in the form of nanopowder aggregates with a primary particle size of 12 nm and a specific surface area of about 150 m² g⁻¹ (Aerosil R7200, Evonik). The organometal precursor was tetraethylorthosilicate (TEOS, Sigma-Aldrich). Methacryloxy(propyl)trimethoxysilane (MEMO, Sigma-Aldrich) was used as a coupling agent. The silica concentration of 20 vol% in the hybrid was formed by 10 vol% of nanoparticles and 10 vol% of silica resulting from the condensation of TEOS. The properties of the hybrid composite are also shown in Table 2. The formulation was shear thinning, with a viscosity 10 times higher than that of the HBP, but 15 times lower than a particulate suspension analog with 20 vol% of silica nanoparticles.[23] The hardness of the hybrid was 71% higher than that of the HBP, and it was also 30% higher than the particulate counterpart.

Table 2: Properties of the HBP and hybrid materials.

Material	Viscosity at 10 rad s ⁻¹ [Pa.s]	Microhardness [MPa]	Refractive index [-]
HBP	0.22	112	1.49
Hybrid	1.93	192	1.48

A 200 W mercury bulb UV lamp (OmniCure 2000, Exfo, Canada) was used to cure the HBP and hybrid materials. The light intensity between 230 and 410 nm was measured using a calibrated radiometer (Silver Line, CON-TROL-CURE, Germany). All samples were irradiated during 3 min. under a UV intensity of 75 mW cm⁻².

AR textures were replicated into the HBP and hybrid materials from a template using a UVNIL tool as detailed in a previous work.[19b] The template was a 20 mm x 20 mm square nickel foil with an hexagonal array of 300 nm high moth-eye based structures (NIL Technology, Denmark). The resin formulation was dispensed on standard glass slides and exposed to UV light under a controlled pressure of 1 bar. 100 microns thick self-standing flat samples were also prepared as references for optical measurements. In the case of the hybrid material, a dual-cure (sol-gel condensation and photopolymerization) process was used.[26] Condensation of the inorganic phase was achieved at 80°C during 4 h, during which photo-polymerization was performed for 3 min. after 45 min. of condensation.

Optical modeling

The optical properties of hexagonal arrays of nanoscopic cones and paraboloids were calculated based on effective medium theory (EMT)[27] using TFCalc.[28] The graded, or effective index of refraction, n_e , of these two geometries was simulated as an equivalent multilayer thin film stack. A total of 45 layers was considered, each layer having an effective index n_e ranging from $n = 1$ (air) to $n = 1.5$ (HBP). Transmittance and reflectance spectra for the multilayer stack were computed from a matrix product, each individual layer being defined by one matrix.[29] The profiles of the effective index n_e were described using Eqn. 1:[11b-d]

$$n_e(h) = \frac{\pi}{2\sqrt{3}} \times \left(1 - \frac{h}{h_0}\right)^\alpha \times (n-1) + 1 \quad (1)$$

where h and h_0 are the height coordinate and maximal height of the feature, respectively. The parameter α is equal to 1 in the case of a paraboloid and to 2 in the case of a cone. In both cases, the base diameter d of the feature was equal to the period p (e.g., no gap between adjacent features), and was fixed to a value of 300 nm. The feature height h_0 was varied from 100 nm (aspect ratio $h_0/d = 1/3$) to 600 nm (aspect ratio 2).

Characterization techniques

The topography of the polymer samples was examined by high resolution scanning electron microscopy (HR-SEM, Zeis Merlin) using an acceleration voltage of 3 kV. The working distance was usually 4.5 mm. In order to avoid any charging effect, the samples were covered with a 7 nm thick

OsO₄ layer. The spectral Reflectance and Transmittance in the visible range was measured using a spectrograph (Oriel-MultiSpec 125™ 1/8 m with Instaspec II™ Photodiode Array Detector with an integrating sphere,^[30] with an accuracy of 0.5% in reflectance and transmittance values.

Solar cells

Amorphous silicon solar cells (a-Si:H, 220 nm thick) were deposited on glass with 2.5 µm thick ZnO front and back contacts.^[31] Micromorph tandem solar cells were also deposited on glass, based on a 230 nm thick amorphous silicon top cell and a 1.3 µm thick microcrystalline silicon (µc-Si) bottom cell, with a 60 nm thick SiO_x reflector in between. Front and back contacts were the same as in the single junction a-Si:H cells.^[32] The AR polymer coatings were detached from the glass slides, prior to be applied on the top of the solar cells. An index matching fluid was used to couple the coatings to the solar cell glass substrate and avoid problems due to e.g. air entrapment.

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