

## Fabrication of a light trapping system for organic solar cells

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### ABSTRACT

Organic photovoltaic cells (OPV) are among the most promising systems for energy extraction and conversion from renewable energy sources. However, major problem to be solved before industrial production could become economically viable is represented by their still low conversion efficiency. The organic solar cell architectures are presently the result of a compromise between achieving complete light absorption using active layers that are thicker than the optical absorption length and achieving efficient charge collection at the electrodes which is favoured in thinner layers. We present a concept and its experimental demonstration that would solve efficiently the above trade-off problem by making use of a new type of light trapping elements. The simple fabrication scheme, based on a self-aligned UV exposure process, suggests its potential up-scalability to large systems, at low production cost.

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### 1. Introduction

One of most interesting and promising class of materials for organic photovoltaics is represented by conjugated polymers [1]. The main advantages of fully organic solar cells are their strong light absorption and easy processability from solution, which would makes production potentially very cost effective. The highest conversion efficiencies have been obtained by mixing donor and acceptor materials to form the so-called bulk heterojunction [2,3].

Light absorption occurs at each of the two material components resulting in the formation of excitons (bound electron hole pairs) [4,5]. The latter are split into free carriers at interfaces, mostly between the donor and acceptor nanophases. After splitting of excitons, holes and electrons proceed towards the respective electrodes through a percolative path by hopping from molecule to molecule of the same chemical species [6]. However, loss mechanism such as exciton decay, charge recombination and low mobility result in reduced photocurrent extraction at the electrodes and low power conversion efficiency.

For the high absorption coefficient of organic materials (exceeding  $10^5 \text{ cm}^{-1}$ ), 100 nm are typically sufficient to absorb most of impinging sunlight. However, unfortunately, this is already about one order of magnitude larger than the diffusion length of excitons

which is typically in the range of 5–10 nm [4,5] and charge recombination length.

A partial solution to the problem of low charge carrier and exciton mobility is represented by the reduction of the active layer thickness, that implies also the loss of a large fraction of the impinging light. The use of a light trapping systems has been actively investigated to increase the total path length of light into the active material without the need of increasing its physical thickness. The concept is to induce sunlight to travel a longer distance in the active layer by multi-pass path in order to exploit most of the radiation. Many different light trapping schemes have been proposed to enhance the quantity of light absorbed in OPV cells such as metal gratings [7], buried nanoelectrodes [8] and scattering [9] and multireflection structures [10–12] are the most proposed solutions. However, the requirement that the feature sizes of the scattering structures be comparable to the film thickness of the OPV cells, i.e., 50–300 nm, and at the same time larger than the wavelength of light to effectively alter the photon propagation direction is intrinsically contradictory. Furthermore, electrical properties can be negatively affected by the introduction of light scattering elements in direct contact with such thin active layers: defects and shorts may easily occur.

The concept of the proposed device (Fig. 1) is that the light focused by an array of microlenses and passing through small apertures is introduced into a cavity delimited by the reflective back-electrode of the cell and the mirror of the trapping system. Once entered the cavity light would bounce back and forth through the active layer with little chance of escaping from it: photons not absorbed at the first pass would be recycled giving them additional chances for being absorbed at a subsequent reflection in the

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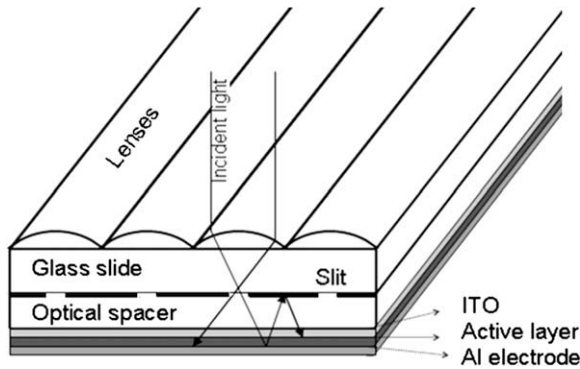


Fig. 1. Schematic representation of the proposed light trapping device.

active film. The system, fabricated on glass or plastics, consists of an array of small openings in a reflective silver film on one side of the substrate and, on the opposite side, of an array of microlenses whose focuses correspond to the position of the openings in the reflective silver layer.

## 2. Experimental methods and results

The fabrication scheme exploits a self-aligned UV exposure to create the pattern of openings aligned to the focus of the microlenses: this process is in principle suitable for up-scalability to large areas with high throughput.

The first step consists of fabricating the mould with an array of inverted (concave) microlenses. The fabrication follows concepts and procedures already described in a previous publication [13]. Briefly, conventional proximity UV-lithography was employed to produce an array of circular holes or straight trenches in a chromium coating on the surface of a fused silica substrate (thickness 3 mm), by patterning a sacrificial positive photoresist Shipley Microposit S1813 resist of 1.5  $\mu\text{m}$  thickness and MF 319 development, followed by Chromium wet etching ( $\text{CH}_3\text{COOH}$ : 35 ml,  $\text{H}_2\text{O}$ : 600 ml, and  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ : 200 g).

Spherical or cylindrical concavities were realized by isotropic wet etching of the fused silica substrates in HF aqueous solution (48% w.), with the openings in chromium acting as the origins of etch. The radius of curvature of spherical or cylindrical concave elements can be easily adjusted by calibrating the etching time. However, during the isotropic etching of fused silica, we observed in general a progressive slowing down of the etching rate from an initial value of 1.1  $\mu\text{m}/\text{min}$ , which we have attributed to the consumption of HF in the etching solution. Therefore, in general the procedure for obtaining concavities with the requested radii of curvature consisted in a first etching step for the duration estimated on the basis of the initial etching rate, followed by a second etching step after the measurement of the actual radii of curvature of the resulting concavities. After reaching the desired etched profile in the fused silica substrate the chromium protective layer was removed by wet etching.

The radius of curvature of the concavities on the mould determine the focal length ( $f$ ) of the polymer microlenses that are obtained in the subsequent process of moulding through the following equation:

$$f = R \frac{n_2}{n_2 - n_1}$$

where  $R$  is the radius of curvature of the lens,  $n_2$  the refraction index of the material of the lenses (that we will assume equal to that of the substrate) and  $n_1$  the refraction index of the external medium (for air,  $n_1 = 1$ ). Before moulding, the fused silica mould has been

functionalized with an antiadhesive coating, by dip in a 5 mM solution of dodecyl-trichlorosilane in heptanes for 30 min.

In order to explore the effect of geometrical parameters on the properties of the final light trapping elements, different types of patterns, namely, gratings of 10  $\mu\text{m}$  wide lines with 200, 250, and 400  $\mu\text{m}$  periods and triangular arrays of dots 8  $\mu\text{m}$  of diameter with center-to-center distance of 80 and 200  $\mu\text{m}$  were tested as the pattern openings in the chromium layer. Correspondingly, cylindrical lenses with periods of 200, 250, and 400  $\mu\text{m}$  and triangular array of spherical lenses with center-to-center distance of 80 and 200  $\mu\text{m}$  were obtained after moulding. The radii of curvature were 350  $\mu\text{m}$  in all cases.

The material for the microlenses was carefully selected among various options. At the initial stage of the device optimization, microlenses have been realized in theOrmocomp resin of theOrmocer family (Micro Resist Technology GmbH); this is an UV curable material for imprinting, designed for manufacturing microstructures like microlenses, optical couplers and connectors or prisms. The quality of the moulded microlenses was very high (with high surface finish, absence of defects such as air bubbles or scratches) and certainly exceeding the requested level for the light trapping system; however, a problem was related to the rather low transparency of theOrmocomp in the near UV, highlighted by the first measurements (Fig. 2). This drawback is particularly relevant for OPC for which the highest absorptance and EQE are in the near UV.

This is the reason for the searching an alternative material, characterised by higher transparency in the short wavelength region. Finally, we selected a UV curable polymer, theNorland Optical Adhesive 73 (NOA 73), which is an optically clear, liquid adhesive that quickly cures when exposed to near ultraviolet light, in the range of 350–380 nm where transparency starts to decay (Fig. 2).

Microlenses have been realized in Norland Optical Adhesive 73 (NOA 73) on glass substrates. As substrate we used a 20  $\times$  20 mm microscope 1 mm thick glass slide, after thorough cleaning in hot acetone and IPA. A drop of NOA was placed on the surface of the master and the latter placed gently in contact with the glass slide, avoiding the formation of air bubbles during this step. An UV mercury lamp with main emission peaks at 350 nm was employed to cure the NOA 73 (Fig. 3a).

In order to reduce the absorption of incident light in the light trapping device, was necessary also in the case of NOA 73 to

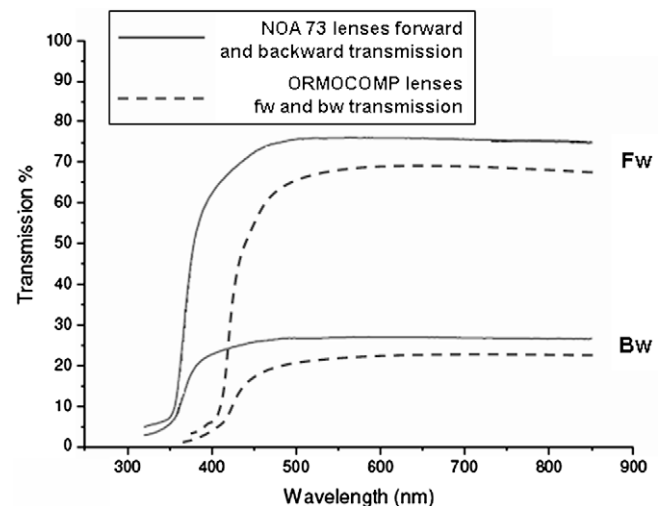
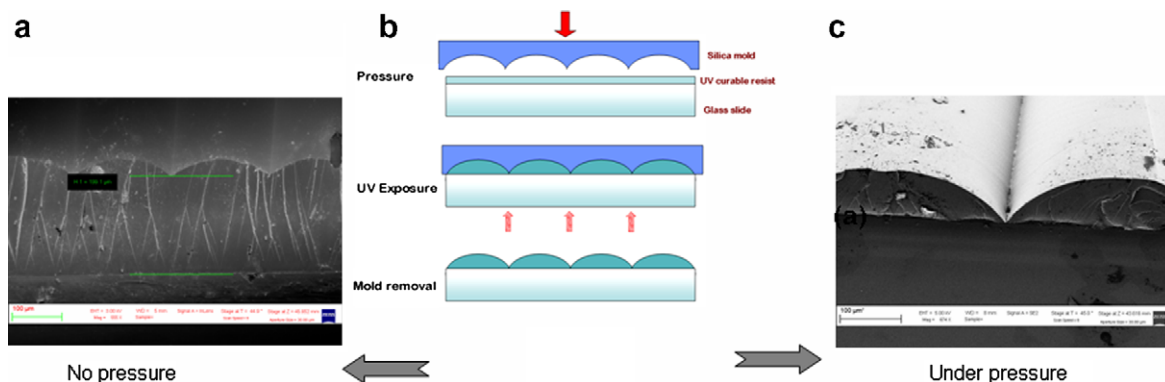


Fig. 2. Forward and backward transmission of 200  $\mu\text{m}$  cylindrical lenses made inOrmocer and NOA.



**Fig. 3.** (a) Schematic representation of microlenses fabrication process. (b–c) The effect of pressure: SEM pictures of cylindrical microlenses obtained applying (b) and not applying (c) the pressure during the exposure.

minimize the thickness of the material of which the optical elements consist. Therefore, during the exposure the mould and the sample were kept together applying a pressure of 1 MPa, in order to obtain a thin residual layer at the base of microlenses, and at the same time ensure the parallelism between the plane of the lenses and that of glass substrate. The effect of moulding the microlenses under pressure is evident comparing the SEM pictures in Fig. 3b–c of two samples made applying and not applying the pressure during the exposure, and resulted in a 8% gain of the forward transmission of light trapping devices.

Finally, NOA 73 was baked for 2 h at 130 °C for complete hardening of the structures: in (Fig. 4) an example of made spherical microlenses.

The next step is that of fabricating a silver mirror on the opposite side of the glass with openings (holes or slits), aligned to the position of the focuses of the lenses. We tested a solution that allowed to bypass the step of alignment and associated problems. Although this step would not represent a challenge for modern technology, would certainly introduce a time consuming step in case of mass production of extended panels in industrial environment. Therefore, we devised a more interesting and perhaps effective fabrication scheme based on a self-aligned maskless UV-lithography process.

The first attempt has been accomplished exposing a positive resist (SPR 220 3.0 thickness 3 mm) through a thin silver film (30 nm) deposited by thermal evaporation on the glass slide (on the opposite side of the lenses): a long exposure was requested, in order to provide the threshold dose to the resist through the semitransparent silver film. The well-defined structures (trenches or holes) obtained in the positive resist film after development, were used as

mask for silver wet etching and thus to create the apertures in the mirror aligned by construction to the lens focuses.

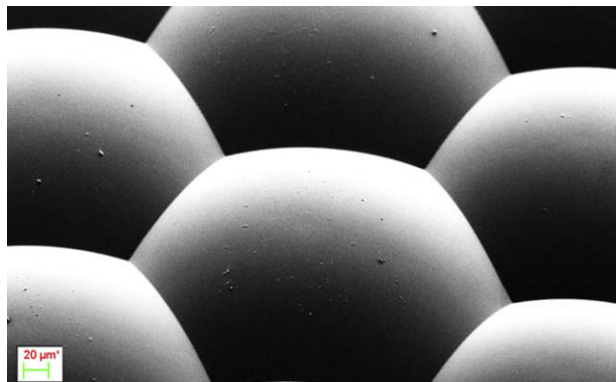
However, the pattern transfer from the resist to the silver film (using a solution of KI and I<sub>2</sub> in water 10:1) was not satisfactory, leading to rough line edges. Moreover, this choice required to limit the thickness of silver to few tens of nanometers, in order to ensure a sufficient exposure of the resist through the metal layer by incident UV-light, although concentrated by microlenses. This scheme has been abandoned, since the presence of a semitransparent mirror therefore results in loss of trapping light efficiency of the device.

For these reasons we moved to a process based on a lift-off with a negative resist. Since negative resists are notoriously not suitable for lift-off process this required to implement the process in a double layer resist system with LOR 10-B (MicroChem) as a bottom layer for the lifting of the top negative resist and the metal evaporated on it. LOR 10-B was spin-coated to a thickness of 700 nm and baked at 190 °C for 5 min as needed. In the baking process the microlenses previously fabricated on the opposite side were kept in contact with the surface of the hot-plate, but no damage was observed on the microlenses as a consequence of this step.

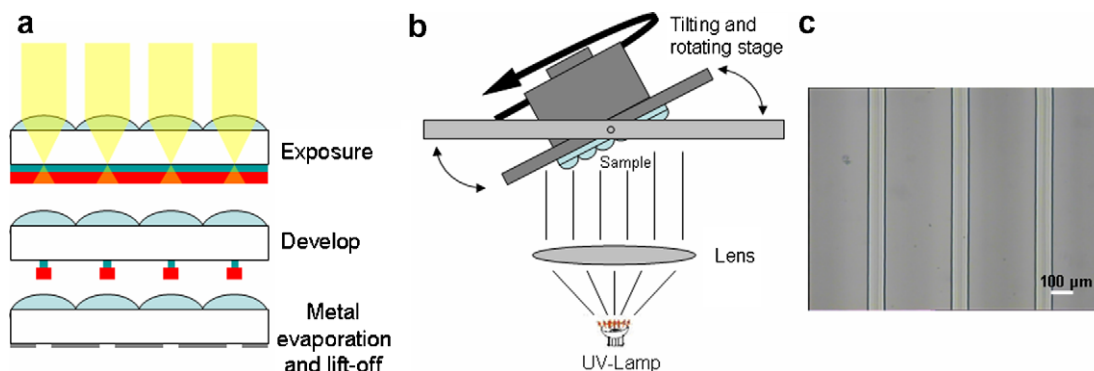
Two different negative resist have been tested: SU-8 (MicroChem) and MR-L6005 (Micro Resist Technology GmbH). The best results have been obtained using the MR-L6005. The SU-8 was more sensitive to stray UV-light due to diffraction effects at the sharp edges between adjacent lenses and multiple reflections at the interfaces, causing the cross-linking of the resist in areas outside the focuses, and difficulties in the subsequent step of metal lift-off.

Therefore, the final devices have been produced using MR-L6005. The resist was deposited by spin coating (at 3500 rpm to produce a 7.5 μm thick film): 150 °C for 5 min and 100 °C for 5 min were, respectively, the pre-bake and post-bake condition set for the processing of the negative resist. Exposure of negative resist was accomplished by a self-aligned process: it consists of a maskless UV exposure that exploits the light focused by microlenses, resulting in a self-aligned structure pattern in the sacrificial resist layers (Fig. 5a).

The light trapping efficiency is strongly correlated to the size of the openings in the mirror. Narrow slits or holes result in a high reflection coefficients, but forward transmission is hampered. Instead, large openings increase the transmission of direct light but the trapping efficiency becomes inadequate. The trade-off can be obtained only by fine control of the size of the openings. For this purpose we have conceived a dedicated solution: the samples were mounted on a rotating stage (Fig. 5b) with the possibility of tilting the rotation axis and the plane of the microlens array with respect to the optical axis of the partially collimated UV source of the mask



**Fig. 4.** SEM picture of spherical lenses of 80 μm period.

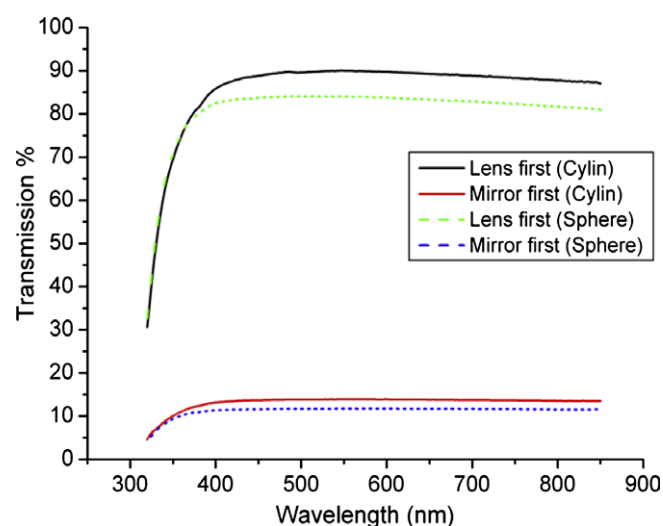


**Fig. 5.** (a) Schematic representation of self-aligned exposure through the microlenses. (b) The rotating stage with the possibility the plane of the microlens array with respect to the optical axis of the collimated UV source. (c) Negative resist structures with improved line edge roughness and controlled feature size.

aligner. By tilting the rotation axis, the illuminated spots describe a circular path of controllable radius, causing the enlargement of the photoresist exposed area; varying the tilt angle allows varying continuously the exposed size of dots or lines (Fig. 6). Furthermore, the rotation, obtained by an electric motor with speed revolution of 60 rpm, allows reducing some negative effects due to chromatic aberrations, UV source divergence and diffraction, thus improving the line edge roughness of the structures produced in the negative resist (Fig. 5c).

Unexposed MR-L 6005 was developed in acetone. An O<sub>2</sub> plasma treatment in inductively coupled plasma (ICP STS) was performed to clean the surface from residuals of the negative resist MR-L 6005 and ensure uniform access of the MF 319 developer to the LOR layer underneath and the formation of a well-defined undercut by controlled shrinkage of it. Final structures (i.e., the patterned mirror) were obtained by metal evaporation and lift-off. A metal tri-layer of chromium, silver and gold has been deposited. The first deposited layer of chromium (5 nm) was introduced for improving the adhesion of the sequent film of silver (150 nm), whereas gold (5 nm) was deposited to prevent the oxidation of silver. After the evaporation, the sacrificial polymer structures and the metal on top were lifted by developing the bottom LOR resist in MF 319.

The main optical characteristics of the light trapping, i.e., optical absorption, transmission and reflection, were measured in the spectral range between 300 and 850 nm wavelength with a Perkin-Elmer Lambda 950 spectrophotometer equipped with a 15 cm diameter integrating sphere. Fig. 7 shows the transmission and reflection curves. Transmission as high as 90% was confirmed in the front direction (light first through the microlenses and then mirror) for cylindrical lenses array of 400 μm period whereas a reflection of >75% was measured for the same sample illuminated with the mirror first. A dip in the forward transmission at wavelength shorter than 380 nm was attributed to absorption in the NOA 73. From Fig. 7, devices made using spherical lenses on an hexagonal array with center-to-center spacing of 200 μm resulted always in a lower forward transmission (by ca. 10%) with respect to those made with cylindrical lenses. We speculate that this evi-

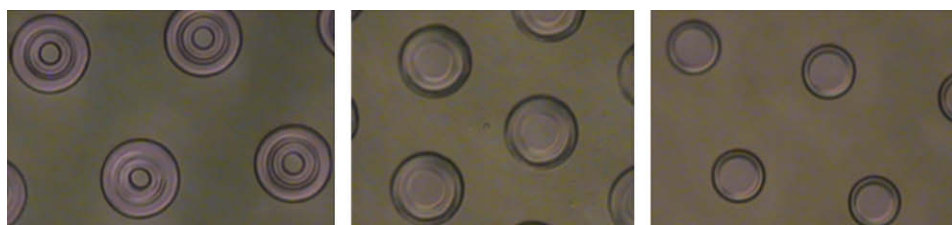


**Fig. 7.** Trap element transmission in the forward and backward direction. The curves referring to light trapping devices with cylindrical lenses array of 400 μm period and spherical of 80 μm period.

dence might be related to two main effects: (1) the intensity of stray light (i.e., the light that falls outside the focus) is larger in the case of spherical lenses which have delimited by an hexagonal perimeter, with respect to cylindrical lenses delimited by straight lines; and (2) we observed a general improvement by increasing the size of the lenses of the same shape and lattice symmetry, that might also be related to diffraction.

### 3. Conclusions

A novel light trapping system for organic solar cells has been presented and an innovative fabrication process using a self-aligned UV exposure through microlenses has been demonstrated.



**Fig. 6.** Control of dimension in dots produced in negative photoresist by exposure at different tilt angles. In the left, the tilt angle was too big, resulting in a doughnut. Filled dots of different sizes are shown in the center and right pictures.



Advantages and problems of the scheme of device implementation have been discussed. Preliminary measurements confirm that the concept was successfully implemented in our device and exhibit good performances both in terms of forward transmittance (90%) and backward reflection (75%). An absolutely fundamental aspect for the effectiveness of this type of light trapping device is that the lenses covers the 100% of the available surface. This is ensured by the adopted scheme of fabrications with moulds made by isotropic wet etching. The same results would have never been obtained with microlenses arrays made with other methods, such as the polymer reflow technique, which leaves 15–20% of the area not covered by lenses.

A first characterization of these elements coupled to organic solar cell showed a relative improvement of their efficiency of up to 25%. This result will be object of a different communication [14].

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