Nano-photonic light trapping near the Lambertian limit in organic solar cell architectures

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Abstract: A critical step to achieving higher efficiency solar cells is the broad band harvesting of solar photons. Although considerable progress has recently been achieved in improving the power conversion efficiency of organic solar cells, these cells still do not absorb upto ~50% of the solar spectrum. We have designed and developed an organic solar cell architecture that can boost the absorption of photons by 40% and the photo-current by 50% for organic P3HT-PCBM absorber layers of typical device thicknesses. Our solar cell architecture is based on all layers of the solar cell being patterned in a conformal two-dimensionally periodic photonic crystal architecture. This results in very strong diffraction of photons- that increases the photon path length in the absorber layer, and plasmonic light concentration near the patterned organic-metal cathode interface. The absorption approaches the Lambertian limit. The simulations utilize a rigorous scattering matrix approach and provide bounds of the fundamental limits of nano-photonic light absorption in periodically textured organic solar cells. This solar cell architecture has the potential to increase the power conversion efficiency to 10% for single band gap organic solar cells utilizing long-wavelength absorbers.

OCIS codes: (050.1950) Diffraction gratings; (240.6680) Surface plasmons; (310.6845) Thin film devices and applications ; (350.6050) Solar energy.

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1. Introduction

Organic solar cells are very promising, rapidly progressing low-cost solar cell architectures. The efficiency of organic photovoltaic (OPV) solar cells has grown rapidly from ~4% to ~10.6% recently [1] by utilizing tandem architectures [2,3] and new absorber layer blends [4]. Photo-electric conversion involves the absorption of light, exciton creation, exciton diffusion, exciton dissociation at the donor-acceptor interface, and migration of free carriers to respective electrodes. Bulk heterojunction (BHJ) films are limited in thickness, since free carrier recombination increases [5] decreasing conversion efficiencies for thicker cells. Poly(3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) OPV cells utilize 100-200 nm thick BHJ films. At these thicknesses the light absorption is incomplete and approaches to increase the optical absorption are necessary. One approach utilizes tandem solar cells that increase the bandwidth of solar absorption. Another approach uses metal nano-particle (NPs) arrays in the electrode or absorber layer [6–10] to generate surface plasmon polaritons (SPPs) within the active layer, where the **E** fields are strongly enhanced, leading to increased light absorption. A 22% improvement of efficiency was found [11] by incorporating Au NPs in *both* the PEDOT:PSS and absorber layers. Recently, organic absorbers were patterned with a 1-d metal-grating back electrode, which increased cell efficiency from 7.2 to 7.73% [12], or with a 1-d embossed PEDOT:PSS [13] that increased the efficiency from 2.74% to 3.35% for a 22% gain. Simulations predict ~23% enhancement by patterning the organic absorber layer together with 2-d metal gratings [14].

A complementary approach to optical enhancement is with *2-d or 3-d* photonic or plasmonic crystals where strong diffraction enhances the path length of light within the

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absorber layer, *in addition* to plasmonic light concentration near the metallic grating [14–16]. This yielded large enhancements in thin film Si-solar cells. A most fruitful concept is the conformal solar cell, where *all* layers of the solar cell grow conformally from a grating surface. We recently discovered a conformal solar architecture using an array of nano-cones that exhibits large enhancements in absorption, theoretically [15] and experimentally [17], in thin film Si cells. This conformal solar architecture enhances the path length of light, creates plasmonic light concentration, and reduces the reflection loss at the top surface of the solar cell, resulting in absorption near the Lambertian limit [18]. Accordingly, we investigate here such a conformal solar architecture for a BHJ OPV solar cell with rigorous simulations. We demonstrate a large *broad-band* absorption increase by >40% using a conformal 2-dimensional patterned organic solar cell architecture, with *both* strong diffraction and light concentration, with absorption approaching the Lambertian limit.

We focus on the process of absorption of light and consequent exciton generation. Simulations utilize the extensively characterized P3HT:PCBM blend as a prototype. The measured wavelength-dependent complex refractive indices $n(\lambda)$ ($n(\lambda) = n_1(\lambda) + in_2(\lambda)$) of P3HT-PCBM [19] indicates strongest absorption at green wavelengths (480-550 nm). The photon decay length is $\zeta(\lambda) = \lambda/4\pi n_2(\lambda)$. $\zeta(\lambda) < 200$ nm in the 480-550 nm region. $\zeta(\lambda) > 200$ nm at shorter λ ($\lambda<480$ nm) and longer λ ($\lambda >600$ nm), and such photons cannot be effectively absorbed within 100-200 nm organic layers, that are smaller than the photon decay length. To improve absorption, light-trapping is necessary at *short* and *long* wavelengths in OPVs, a key difference from Si-films- where *long* wavelength light trapping is necessary.

A relevant comparison is the Lambertian or Yablonovitch limit [18] where the light is stochastically randomized within the absorber layer and the path length is enhanced by a factor of $4n(\lambda)^2$ in the the weak absorption limit [20]. Light randomization results in uniform population of modes, and a spherical phase space of occupied photon modes [21] in **k**-space. The Lambertian $4n^2$ limit was considered to be the best achievable for light-trapping. However, recent theories suggested that this limit may be approached and overcome. Using a conformal solar cell with a periodic back-reflector [22] we showed that the $4n^2$ limit is approached in thin film Si over the *entire* spectral range. Yu et al [23] predicted that the $4n^2$ limit can be reached or surpassed over a broadband, in thin low index organic absorber layers ($\varepsilon = 2.5$) [23] using a complex surface structure. Simulations have argued for surpassing the broad-band Lambertian limit with double-layer photonic crystal cavities [24], and nano-rod arrays [25] in c-Si. Schiff showed [21] that SPPs in back-reflectors generate enhancement over the $4n^2$ limit, near the SPP frequency. $4n^2$ is much lower (~12-13) in organics than 45-50 in silicon. We show here that a conformal OPV solar cell utilizing a photonic crystal can approach the Lambertian limit over the *entire* spectral range of interest.

2. Theoretical basis

The simulated solar cell architecture (Fig. 1) has a thick glass substrate, coated with a 2 dimensional *patterned* indium tin oxide (ITO), of thickness d_1 and a corrugation of height d_2. This may be experimentally achieved with micro-transfer molding or soft lithography. On this two-dimensional photonic crystal (PC), a conformal solar cell is modeled. In practice there is a thin PEDOT:PSS layer (<30 nm) between ITO and the organic absorber. Since the optical properties of this layer are similar to ITO we simplify the model and do not include it in our calculations. We coat this texture with a P3HT-PCBM layer (thickness d_3), and a silver back reflector cathode. *All layers* assume the periodic texture of the substrate, as found in conformal growth The corrugation height at the metal-organic interface d_4 can be smaller than d_2. Measured complex $n(\lambda)$ are used for Ag [26], and ITO [16]. Alternatively a periodically textured polymer substrate, as utilized for Si cells [17], could be used. Spin coating an organic layer on a patterned substrate and maintaining uniformity of coatings is very challenging [27]. We adopt the constraint that the depth of the corrugation is less than the thickness of the organic film- which is likely for fabrication.

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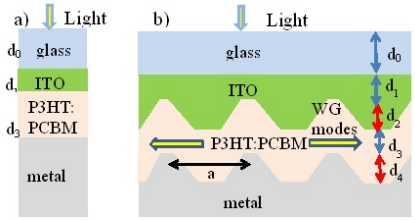

Fig. 1. a) Flat cell and b) conformal solar cell architecture.

We use the scattering matrix (SM) method [28] where Maxwell's equations are solved in Fourier space, i.e. in a basis of plane waves for both polarizations. The solar cell (Fig. 1) is divided into layers in the z-direction. Within each layer the dielectric function is a periodic function of x and y. Maxwell's equations are integrated with continuity boundary conditions through the cell to obtain the SM of the entire structure. We obtain the total reflectance R (including diffraction), transmission T (~0) and absorption A = 1-R-T at each λ. This SM technique has advantages over real-space methods of being able to simulate fully 3-d geometries, without added memory requirements, since a real space grid is unnecessary. The SM method is easily parallelized with each frequency being sent to a different processor [15]. We characterize solar architectures by their broad-band absorption $<A_w>$, weighted by the AM1.5 solar intensity dI/dλ, and the idealized short circuit current, where

$$< A_w >= \int_{\lambda_2}^{\lambda_1} A(\lambda) \frac{dI}{d\lambda} d\lambda, \tag{1}$$

$$J_{sc}^{\max} = \frac{e}{hc} \int_{\lambda_2}^{\lambda_2} \lambda A(\lambda) \frac{dI}{d\lambda} d\lambda. \tag{2}$$

Ideal internal quantum efficiency is assumed. The spectral range of absorption is from 400 nm to 700 nm appropriate for P3HT-PCBM with a HOMO-LUMO splitting of 1.77 eV. We employ conical arrays, in a triangular lattice, which yielded high absorption enhancements in Si-based solar cells [15, 17]. Convergence was easily achieved with ~330 plane waves for each polarization or a matrix size of 660. To compute the organic layer absorption only we do not use absorption within the ITO, and use nearly ideal loss-less metal [29].

2. Results

We optimize the structure of the conformal solar cell by starting with a 100 nm P3HT:PCBM layer and varying the pitch a and height d_2 of the 2-d triangular lattice photonic crystal (PC) grating. The optimized structure has highest absorption and photo-current for a pitch a~600 nm, and a grating height of 90-100 nm (Fig. 2(a)). $<A_w>$ and J_{sc} as a function of the pitch (Fig. 2(b)), for the fixed corrugation height d_2 = 90 nm, shows the absorption is considerably enhanced by ~40% and the photo-current by ~50% relative to a flat (190 nm) P3HT-PCBM film with the same amount of organic material as in the corrugated film. These enhancements exceed those from patterning a single interface [14]. J_{sc} is more enhanced that the weighted $<A_w>$ since J_{sc} (Eq. (2) preferentially weights longer λ where more enhancement is found. The enhancement is further increased to ~100% for thinner 60 nm organic layers. The conical pillars with a base radius R have the highest absorption for an optimized radius R/a≅0.36-0.4 since the largest Fourier component of the scattering potential is $2J_1(GR)/GR$, where J_1 is the first order Bessel function. For the triangular lattice the lowest $\mathbf{G}_1 = (2\pi/a)(1,-1/\sqrt{3})$, the largest scattering potential occurs near R/a~0.35 [28], corroborating the numerical results. When the height d_4 of the metal-side corrugation is smaller than the corrugation height d_2 at the ITO, as expected in conformal growth, the photo-current and enhancement decrease nearly linearly with d_4 (Fig. 2(c)), for different pitch values, due to decreased plasmonic enhancements at the metal-organic interface Having nearly equal corrugation heights (d_2 = d_4), is desirable.

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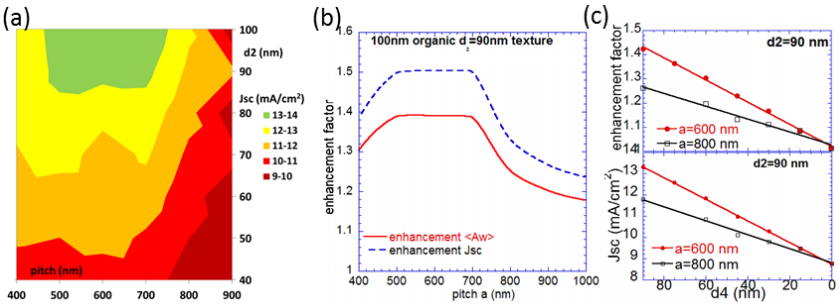

Fig. 2. a) Simulated photocurrent as a function of the pitch a and height d_2 of the periodic corrugation b) Enhancement factor of the absorption and the photo-current as a function of the pitch, with a corrugation height of 90 nm, relative to a flat 190 nm cell. c) J_{sc} and enhancement when the height d_4 of the metal corrugation differs from the ITO corrugation (for the optimal d_2 = 90 nm) and 600/800 nm pitch.

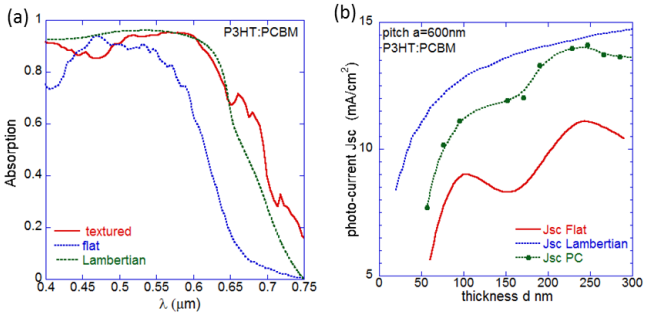

Fig. 3. a) Wavelength-dependent absorption for the periodic textured cell, flat cell and the Lambertian limit. All cells have the same absorber volume. b) Simulated photo-current as a function of the absorber layer thickness compared to the same limits.

The absorption (Fig. 3) is strongly enhanced at most wavelengths for the conformal patterned organic solar cell, relative to the flat case. Substantial enhancements occur at short and long wavelengths (λ <480 nm; λ >600 nm), where photon decay lengths exceed the absorber layer thickness. The oscillatory absorbance is due to multiple interference effects from the thick (700 μm) glass substrate. The absorbance approaches the Lambertian limit for wavelengths λ ~600 nm, and is distinctly higher than the Lambertian limit for λ >600nm. There may be residual absorption of the metal at long λ where the organic is not absorbing.

4. Discussion and conclusions

Wave-guided modes (Fig. 1) propagate in the plane of the absorber, when the roundtrip phase difference $\Delta\phi$ from the top and bottom of the absorber layer is a multiple of 2π ($\Delta\phi = m2\pi$). Then $k_z = m\pi/d$, where d is the absorber layer thickness. The RLVs **G**, have $G_x = i(2\pi/a)$ and $G_y = (2j\text{-}i)(2\pi/a)/\sqrt{3}$ in the triangular lattice where (i,j) are integers. Incident light with wave-vector $\mathbf{k}_{||}$ is diffracted according to $\mathbf{k}_{||}' = \mathbf{k}_{||} + \mathbf{G}$. Since $k_z = m\pi/d$, and $k_z^2 + k_{||}'^2 = n(\lambda)^2(\omega/c)^2$, wave-guiding occurs at the resonant wavelengths

$$\lambda(i,j,m) = 2\pi n(\lambda)/[i^2 + (1/3)(2j-i)^2)(2\pi/a)^2 + (m\pi/d)^2]^{1/2}, \qquad (3)$$

specified by three integers (i, j, m). The structure is optimized so that a dense mesh of resonant wave-guided modes occurs in the wavelengths of interest. The J_{sc} as a function of the thickness (Fig. 3(b)) is strongly enhanced over the flat cell. The conformally textured cell has approached the Lambertian limit (Fig. 3(b)) for the photocurrent, for 200-250 nm thickness.

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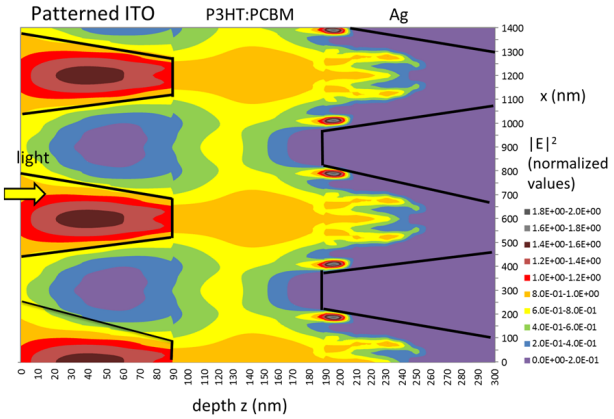

Fig. 4. Electric field intensity $|E|^2$ in the cross section of the organic solar cell at $\lambda = 620$ nm.

The electric field intensity $|E|^2$ in a cross section is plotted in Fig. 4, at 620 nm. The **E** fields penetrate deep into the cell, in this weak absorption regime. Incident light is focused in the front of the cell, in the ITO layer, and in the P3HT-PCBM directly below the ITO nano-cone- which enhances absorption. SPPs enhance the field intensity by a factor of ~2 at organic-metal interface, in sub-wavelength regions adjoining the conical metal nano-pillars, giving rise to strong absorption in P3HT-PCBM adjacent to the cathode. SPPs and wave-guided modes couple in this conformal solar architecture [15, 22]. The SPP intensity enhancement of ~2 in these organic layers (n~1.8-2) is smaller than the ~6-7 found in Si [15, 22] (n~3.6) since SPPs are less spatial localized with the lower index n. There is substantial wave-guiding within the ITO layers, that reduces the confinement within the organic layer [30], reducing the Lambertian limit from $4n^2$.

High light intensity enhancements from SPPs, increase the local electric fields that can increase the exciton dissociation at donor-acceptor interfaces. It is preferable to keep the interlayer between the organic absorber and the metal cathode very thin (e.g. 1 nm LiF), so that the plasmonic intensity maximum occurs primarily within the absorber. Patterning the entire solar cell in a conformal architecture provides larger enhancements and diffraction, than patterning the organic absorber layer alone, where broad-band enhancements of 23% have been predicted [14]. The triangular lattice generally provides stronger diffraction and enhancements [22] than the square lattice. For P3HT:PCBM the power conversion efficiency could be enhanced from ~4% to ~6% if full light trapping is achieved. We expect similar enhancements of ~50%, for organic polymers, such as PTB7, that absorb at longer wavelengths and have 7-8% power conversion efficiency. Thus this solar architecture has the potential for *single junction* organic solar cells *exceeding* 10% power conversion efficiency.

We developed a conformal organic solar cell architecture with large enhancements of optical absorption of ~40% and photocurrent of ~50% for common absorber layer thicknesses. These enhancements exceed those from patterning the organic metal cathode interface alone. The absorption approaches the Lambertian limit. A gentle 80-90 nm corrugation discussed here may be at the feasibility limit for solution processing. Our simulation provides important bounds of the fundamental limits of nano-photonic light absorption. The Lambertian limit may represent a limiting stochastic absorption value independent of material.

Acknowledgments

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