Plasmonic concentrators for enhanced light absorption in ultrathin film organic photovoltaics

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We report on experimental absorption enhancement in 24 and 150-nm-thick bulk heterojunctions of the conducting polymer poly(3-hexylthiophene) and the fullerene (6,6)-phenyl C_{61} butyric acid methyl ester. By using periodic and quasiperiodic hole arrays as nanoengineered plasmonic concentrators milled in a silver film, a spectrally broad, omnidirectional, and polarization-insensitive absorption enhancement is observed over that of a reference layer deposited on a flat film. As the result of increased absorption, an enhancement in the polymer fluorescence intensity is also observed. This demonstrates the potential of plasmonic concentrators for improved energy harvesting in ultrathin film solar cells. © *2011 American Institute of Physics*.
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In conventional solar cells, the active layers are optically thick to absorb most of the incident sunlight, and at the same time they must be crystalline and pure to allow for efficient photocarrier collection. Methods to reduce the active layer thickness by several orders of magnitude (from 10–100 μm down to 10–100 nm) would significantly expand the range and quality of absorbing materials suitable for photovoltaic devices. Thin-film photovoltaics offers the possibility for low-cost fabrication of solar cells, a noteworthy example being organic photovoltaics (OPVs).[1] Power conversion efficiencies of about 4% have been recorded for OPVs using a bulk heterojunction of the conducting polymer poly(3-hexylthiophene) (P3HT) and the fullerene (6,6)-phenyl C_{61} butyric acid methyl ester (PCBM) as the active layer.[2,3] However, despite a promising steady increase in performance levels, the highest power conversion efficiency reported so far is of the order of 7% for single-junction, state-of-the-art organic solar cells.[4]

This low performance originates from the relatively low mobility of photogenerated charge carriers and short exciton diffusion lengths in P3HT, ranging from 4 to 12 nm.[5,6] While recombination losses can be dramatically reduced in thinner films (<30 nm), the drawback is the exponential reduction in absorption of incident photons. It would therefore be beneficial to consider methods for enhancing absorption in ultrathin films, such as the excitation of surface plasmon polaritons (SPPs).

While several plasmonic structures and strategies have been suggested as potential candidates for enhanced energy harvesting in thin-film solar cells,[7] most recent research activity has focused on the use of metal nanoparticles deposited on the top surface of a solar cell.[8–12] Other approaches use nanometer-scale metallic gratings[13,14] and grooves[15,16] to enhance absorption of light with a specific polarization, by causing light to diffract from its original direction and propagate parallel to the metal-dielectric boundary in the form of SPPs.[15,17] Therefore, light coupled to the SPPs can travel a much greater distance than the thickness of the absorbing layer, potentially leading to increased absorption even in optically thin layers.

Recently, deterministic aperiodic arrays of gold nanoparticles have been shown to exhibit interesting properties such as localized modes, photonic band gaps, and broadband light scattering, as the result of the collective behavior of localized plasmon resonances.[18–20] These aperiodic structures have been proposed for applications such as surface enhanced Raman scattering[18] and improved sensitivity to refractive index change for label-free biosensing[19] but could find applications for enhanced scattering and absorption efficiencies in solar cells.

Here we investigate the role of quasiperiodic arrays of nanometer-scale holes milled in metal films as effective plasmonic concentrators for enhanced efficiency in thin-film solar cells.

Hole arrays were generated using a generalization of the "cut-and-projection" method originally proposed by de Bruijn, to tile the plane according to quasiperiodic distributions of points.[21,22] Our algorithm uses a distribution of points obtained by the intersection of an N-fold cubic lattice space with a two-dimensional (2D) plane and projection of the closest lattice points onto the plane. The set of projected points generates 2D tilings of the plane, such as those reported in Fig. 1.

We calculated the SPP propagation length at the P3HT:PCBM/Ag interface, using experimentally measured dielectric constants for the bulk heterojunction and for plain silver. The SPP propagation length is 50 nm for incident wavelengths between 400 and 550 nm, and then exponentially increases to 100 at 580 nm, and up to 1 μm at 680 nm. Therefore, we expect plasmonic concentrators to be more effective when designed for enhancement at longer wavelengths, >550 nm.

Focused ion beam (FIB) milling was used to pattern 300 nm thick silver films with holes 80 nm in diameter and 70 nm deep, to form 100 μm × 100 μm arrays with a hole–hole separation distance of 400 nm. This distance has been chosen to optimize absorption at a wavelength of 580 nm in all hole arrays, based on our understanding and modeling of the universal optical behavior of hole arrays.[23] In so doing, we hoped to understand the role of periodicity and quasip-

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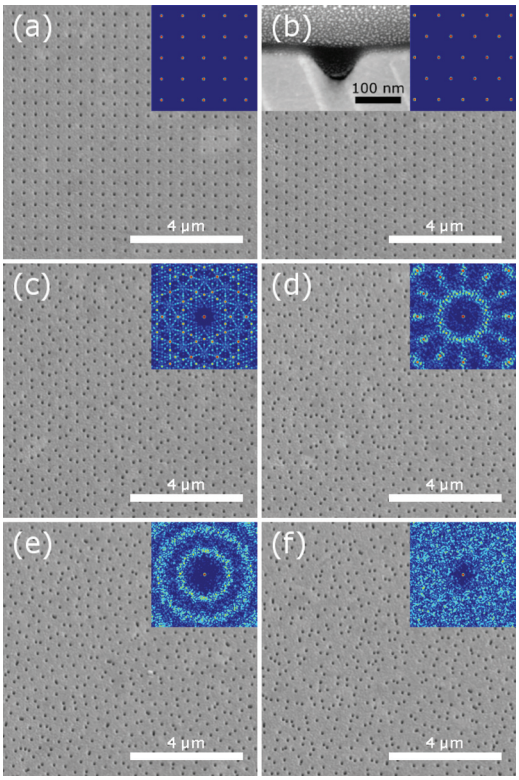

FIG. 1. (Color) SEM micrographs of periodic [(a) square, (b) triangular], quasiperiodic [(c) penrose, (d) dodeca-grid, and (e) heptadeca-grid], and (f) random hole arrays milled in a 300-nm-thick silver film. The insets show the 2D discrete Fourier transform power spectra for each array. The left inset to (b) shows a high-resolution cross sectional SEM micrograph of a polymer-filled hole in the triangular array.

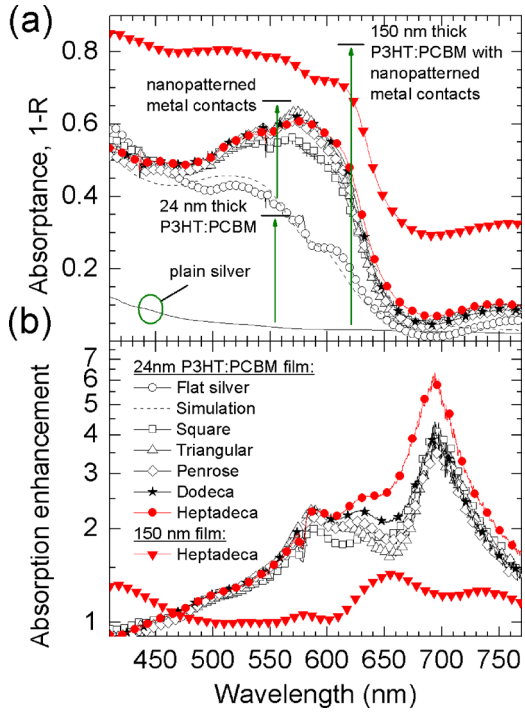

FIG. 2. (Color online) (a) Absorptance spectra (defined as 1-R(λ), R(λ) being the experimental reflectance), for P3HT:PCBM films spin-cast on unpatterned and patterned silver. (b) Absorptance spectra for P3HT:PCBM films on various patterns, normalized to the spectra of equally thick films on unpatterned silver.

eriodicity in the absorption enhancement. Thus, for each array we also fabricated a corresponding reference array with the same number of holes but with randomized position.

P3HT and PCBM were dissolved in dichlorobenzene at 50 °C with 1:1 weight ratio and 10 mg/ml concentration each, then spin-cast (5000 rpm, 60 s) onto the silver film. The resulting 24-nm-thick polymer films were dried at room temperature in a covered Petri dish for 20 min, then annealed at 110 °C for 10 min. For comparison, we also spin-coated a 150-nm-thick film (1000 rpm, 60 s) on an identical patterned silver substrate.

Sample reflectance and fluorescence measurements were taken using a Nikon Eclipse Ti optical inverted microscope, with a high numerical aperture objective (40×, NA=0.6) for both excitation and collection. An unpolarized broadband light source was used to illuminate the sample. Light intensity was then collected through the same objective, dispersed using a spectrograph, and detected with a digital charge-coupled device camera system.

Figure 1 reports on scanning electron microscope (SEM) micrographs of periodic (square and triangular), quasiperiodic (Penrose, dodeca-grid, and heptadeca-grid), and a randomized hole array. The inset to Fig. 1(b) shows a high resolution cross-sectional SEM micrograph of a representative polymer-coated hole in a triangular array. Prior to FIB milling, we performed *in situ* electron-beam assisted deposition of a Pt protective layer (top layer in inset) to prevent damage to the polymer film. From the micrographs we inferred the film thickness (uniformly 24 ± 2 nm between holes and in unpatterned regions) and hole diameter and depth. Additional insets show the 2D discrete Fourier transform power spectra for each array. The quasiperiodic hole arrays are characterized by unusual Fourier transforms, as the result of local and long-range order and the absence of translational periodicity. Of particular interest is the heptadeca-grid array [Fig. 1(f)], which shows broad, diffuse diffraction rings in its Fourier transform power spectrum. These rings suggest the possibility of achieving omnidirectional and polarization-insensitive light scattering.

In order to estimate the fraction of absorbed energy in the thin polymer film, we performed reflectance measurements, and from the reflectance spectra R(λ) we derived the optical absorptance A(λ)=1-R(λ) in the polymer, as reported in Fig. 2. Upon introduction of a 24-nm-thick P3HT:PCBM film, the absorptance increases from ~5% to 35% at 520 nm. The dashed line is a fit to the absorption data using a multiple reflection model. The inferred thickness of 24 nm obtained by the fit is in agreement with the experimentally determined value using cross-sectional SEMs. Figure 2(a) also shows that the absorptance can be increased to 55%–65% due to the presence of plasmonic concentrators in the same film. The absorptance can be further increased to about 80% using the thicker (150 nm) polymer film.

To better understand the role of the plasmonic concentrators, we evaluated the experimental absorption enhancement factor, relative to a layer of the same thickness on a flat silver film. The results are shown in Fig. 2(b). For the 24-nm-thick film, relative absorption enhancements greater than 100% are observed over a broad spectral range from 450–800 nm, with peaks of ~240% observed at 590 nm, and up to ~600% at 700 nm. The thicker film is already a strong absorber in the wavelength range 470–600 nm, where the extinction length is comparable to the film thickness, there-

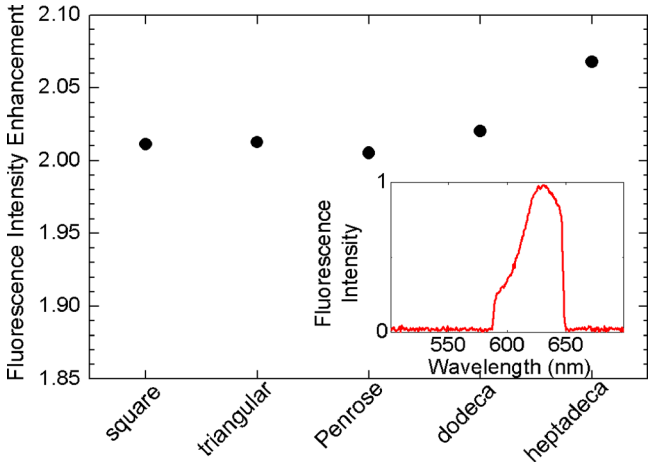

FIG. 3. (Color online) Fluorescence intensity of a 24 nm P3HT:PCBM film spin-cast on silver with various plasmonic concentrators, normalized to the emission of the same film on unpatterned silver. The excitation wavelength was 550 nm. The inset shows the filtered fluorescent emission spectrum for a square pattern.

fore the plasmonic enhancement is not significant. However, at wavelengths shorter than 470 nm and longer than 600 nm, where the absorption coefficient is reduced, plasmonic concentrators can enhance absorptance up to 150%. Among the different structures, the quasiperiodic array designed according to the heptadeca-grid method seems to be the most promising plasmonic concentrator. We attribute this to the associated broad, diffuse diffraction rings, causing a more polarization- and angle-insensitive response to the incident light. In addition, the maximum relative absorption enhancement for the periodic and quasiperiodic arrays, compared to their respective randomized arrays (not shown), occurred at 580 nm as by design.

In support of the observed absorption enhancement, we also performed epifluorescence imaging and spectroscopy, using a dichroic filter and emission filter for 550 nm excitation and 625 nm emission wavelengths. A typical filtered fluorescence spectrum for a 24-nm-thick film is reported as an inset to Fig. 3. The solid circles report the measured fluorescence intensity enhancement in the presence of various plasmonic concentrators, normalized by the intensity coming from a nearby region without patterns. We observed a twofold enhancement of the fluorescence intensity, consistent with the absorption enhancement at the excitation wavelength. We estimate that material filling the holes accounts for only 5% of the total absorber volume; therefore, the observed twofold absorptance enhancement can be exclusively ascribed to plasmonic effects.

Finally, we performed an analysis of the theoretical efficiency enhancement due to the increased absorptance in the presence of plasmonic concentrators, using air mass 1.5 illumination conditions. We estimate a 46% enhancement in total power density absorbed (from 130 to 190 W/m^2) by 24 nm P3HT:PCBM thin films with plasmonic concentrators and an 11% enhancement (from 280 to 310 W/m^2) in 150 nm films. High absorption enhancements in films whose thickness is lower than or comparable to the exciton diffusion length could lead to overall higher external quantum efficiency, due to the improved transport properties of ultrathin films compared to optically thicker films. Plasmonic concentrators are also effective in thicker films, at those wavelengths where the absorption coefficient is reduced.

In conclusion, we showed broadband absorption enhancement of unpolarized, diffuse white light using plasmonic concentrators coated with thin films of organic absorbing material. For a 24-nm-thick film, a twofold absorption enhancement was measured at an incident wavelength of 580 nm, with peak enhancement of ~600% at 700 nm. In correspondence, we observed a twofold enhancement in fluorescence intensity as the result of increased excitation rate. Absorption enhancements of up to 150% were also observed in a 150-nm-thick film at wavelengths longer than 600 nm. The results reported suggest the potential of plasmonic concentrators as a viable method to enhance efficiency in thin film photovoltaic cells.

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