Self-assembled plasmonic electrodes for high-performance organic photovoltaic cells

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We investigate thin Ag films incorporating plasmonic nanohole arrays as transparent conducting electrodes for organic photovoltaic cells. Plasmonic electrodes are fabricated using nanosphere lithography to create hexagonal nanohole arrays over centimeter-sized areas. Devices constructed using a nanopatterned Ag anode show power conversion efficiencies that exceed those of devices constructed on conventional indium-tin-oxide, independent of light polarization. In comparison to cells constructed on unpatterned Ag, the power conversion efficiency is noted to double with patterning. © 2011 American Institute of Physics. [doi:10.1063/1.3635385]

Plasmonic photovoltaic cells aim to harness surface plasmons (SPs) for capturing light and enhancing optical absorption for efficient photoconversion. Surface plasmons are electromagnetic waves confined to the surface of a metal-dielectric interface as a result of coupling to the conduction electrons in the metal.¹ Evanescent SP waves are generated when light scatters from subwavelength metallic features and permit the manipulation and enhancement of optical fields well below the diffraction limit.² Interest in plasmonic nanostructures has increased recently due in part to the development of new technologies to nanopattern thin metallic films.^{2,3} Various plasmonic nanostructures have been integrated in photovoltaic cells to exploit SPs for increased optical absorption by resonantly enhancing the local field or redirecting incident light to increase the optical path length.^{4–8} Plasmonic nanostructures are particularly useful in organic photovoltaic cells (OPVs) where absorption leads to the formation of excitons, which must diffuse to a dissociating heterojunction in order to contribute to the photocurrent.⁹ The absorbing layers in OPVs are typically kept necessarily thin since the exciton diffusion length is small $(\sim 10 \text{ nm})$, limiting the absorption efficiency.¹⁰

The integration of plasmonic structures with OPVs has been previously examined using metallic nanoparticles^{11,12} and patterned metal films.^{4,5} An advantage of using continuous metal films for the excitation of SPs is their ability to replace conventional transparent conducting materials and serve as a device electrode. Thin metallic films are able to show both high conductivity and optical transparency at reduced thickness, while also being amenable to nanostructuring and patterning. Previous reports have employed metallic films in light trapping arrangements to enhance optical absorption in both organic and inorganic photovoltaic devices.^{13,14} While promising, many of these reports have shown device efficiencies below those of cells constructed using conventional electrodes. These lower efficiencies could be attributed to the use of relatively thick metal films that block a significant portion of the incident photon flux^{4,5} and a polarization dependence that arises when one-dimensional gratings are used.^{4,15} Therefore, it is desirable to construct transparent plasmonic electrodes using thin, nanostructured metal films with polarization-insensitive properties.

While previous work on plasmonic nanostructures has often involved electron-beam lithography, focused ion beam milling, interference lithography, or nano-imprint lithography, the cost of patterning nanohole arrays over large areas becomes a significant bottleneck for low-cost applications. To address this challenge, we employ a colloidal self-assembly technique known as nanosphere lithography (NSL). The NSL technique is attractive as it does not require a photomask or imprint mold, eliminates high capital cost lithography, and provides a high-throughput, tunable, substrate-independent nanostructure over a large area.^{16,17}

Nanopatterned Ag films were fabricated using selfassembled polystyrene nanospheres having a diameter of 400 nm. Nanosphere solutions were deposited onto a glass slide and dried within a polydimethylsiloxane ring having a diameter of 2 cm. The size of the close-packed nanospheres was reduced with a reactive ion etch process in an O₂ plasma. To form the electrode, a thin Ag film was deposited onto the surface using high vacuum thermal evaporation. Hexagonal nanohole arrays were obtained by removing the polystyrene beads with sonication in dichloromethane. Overall, single-crystalline domains of ~10 μ m × 10 μ m were obtained with larger areas consisting of adjacent singlecrystalline grains forming polycrystalline films.

Nanostructured Ag films were integrated into OPVs, and performance was characterized as a function of Ag film thickness to determine optimum electrode conditions. It was found that for Ag film thicknesses >12 nm, the electrical performance of the patterned electrode is maintained. Broadband optical transmission spectra for both patterned and unpatterned Ag films having thicknesses (hole sizes) of 12 nm (250 nm), 16 nm (200 nm), and 20 nm (175 nm) are shown in Fig. 1. The hole size increases as the Ag thickness

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FIG. 1. Measured transmission spectra for ITO, (a) 12 nm, (b) 16 nm, and (c) 20 nm Ag films on a glass substrate. The transmission increases uniformly with decreasing Ag thickness and spectral features arise due to patterning. Patterned films exhibit a dip and a peak in the transmission due to the excitation of surface plasmons.

is decreased due to the spherical shape of the nanosphere. The transmission spectrum of indium-tin-oxide (ITO) is also shown for comparison. A significant increase in transmission is observed at wavelengths $(\lambda) > 600$ nm upon patterning with hexagonal hole arrays having a 400 nm periodicity. Theoretical studies have shown that peaks in the enhanced optical transmission for square hole arrays increase in intensity and shift to longer wavelengths as the thickness of the metal film approaches the skin depth due to the coupling of light with short-range SPs.¹⁸ The optical transmission spectra of the hexagonal hole arrays used in this work also show the same qualitative behavior and exhibit a broad transmission peak in the near-infrared region. The results shown in Fig. 1 demonstrate that even in Ag films as thin as 12 nm, nanopatterning and the resulting plasmonic effects can enhance the optical transmission. However, simple far-field optical transmission measurements do not capture the local field enhancement mediated by SPs. In fact, the excitation of bound SP modes in the metal film can lead to decreased optical transmission at the excitation wavelength,⁵ and finite-difference time-domain (FDTD) simulations confirm highly localized fields are present even at the transmission minimum. Therefore, fully integrating patterned anodes with OPVs is the only way to determine the increased internal plasmonic field and the impact on power conversion efficiency.

To characterize the performance of nanopatterned Ag films as plasmonic electrodes, devices were fabricated on unpatterned and patterned Ag electrodes as well as on conventional ITO substrates (15 Ω /sq.). All ITO substrates were degreased with detergent and solvents and exposed to a UV-ozone ambient just prior to the deposition of the organic active layers. Organic layers were deposited by high vacuum thermal sublimation (<10⁻⁷ Torr) at a rate of 0.2 nm s⁻¹. A 20-nm-thick electron donor layer of copper phthalocya-



FIG. 2. Device performance parameters under AM1.5G simulated solar illumination. (a) Comparable values for the open-circuit voltage (V_{OC}) and fill factor (FF) are obtained using all anodes, demonstrating comparable electrical performance. (b) Devices with a patterned anode show the highest responsivity due to the plasmonic field enhancement. (c) The increased responsivity of the patterned device leads to a higher power conversion efficiency relative to devices using either an ITO or unpatterned Ag anode.

nine (CuPc) was deposited directly onto the anode, followed by a 40-nm-thick electron acceptor layer of C_{60} , and a 10nm-thick layer of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) which serves as an exciton blocking layer.¹⁹ A 50-nm-thick Al cathode layer was deposited at a rate of 0.3 nm s⁻¹ through a shadow mask defining a circular active area having a diameter of 1 mm.

Devices were characterized under AM 1.5G solar simulated illumination. Figure 2 compares data collected from devices constructed on ITO and those constructed on Ag anodes having a thickness of 12 nm. The performance of the ITO-based OPVs is consistent with previous reports using similar film thicknesses.^{20,21} The open-circuit voltage (V_{OC}) and fill factor (FF) are comparable for all three electrodes, demonstrating that the nanopatterning does not adversely affect the electrical properties of the anode (Fig. 2(a)). The main performance difference with patterning is in device responsivity (Fig. 2(b)). Devices fabricated on patterned Ag show a larger responsivity than that those on ITO even though transmission through the bare electrode is lower than that of ITO. This difference comes from the excitation of SPs along the metallic electrode. Consequently, the power conversion efficiency for devices fabricated on patterned Ag is larger than that measured for devices constructed on ITO and is almost twice that obtained for devices constructed on unpatterned Ag (Fig. 2(c)). Device response was found to be independent of light polarization, in contrast to previous work containing linear metallic gratings.⁴

Figure 3 shows external quantum efficiency (η_{EQE}) spectra for devices constructed on ITO as well as on patterned and unpatterned Ag films with a thickness of 12 nm. All devices show comparable η_{EQE} for $\lambda < 500$ nm. The spectra begin to diverge for $\lambda > 500$ nm due to the generation of SPs (Fig. 1). For such wavelengths, the spectral response for the patterned Ag anode device is larger to that of both the unpatterned and ITO devices. Increased response for the



FIG. 3. External quantum efficiency (η_{EQE}) for devices with anodes consisting of ITO and 12 nm unpatterned and patterned Ag. The η_{EQE} increase for devices with a patterned anode at wavelengths larger than 500 nm reflects the enhanced absorption in the CuPc donor arising from spectrally broad plasmonic contributions at the anode-donor interface.

unpatterned device corresponds to the region of high optical absorption for CuPc due to the large local field enhancement generated near the patterned metal anode.

The electromagnetic field distribution of the entire device was visualized using full 3-D FDTD calculations. Material constants were obtained via ellipsometry for the organic layers and from Rakic²² for the metals. Figure 4 shows simulated, time-averaged cross-sectional field intensity maps at an incident wavelength of 622 nm, close to the absorption maximum of CuPc. Figure 4(a) shows a reference field map for a device which has a 12 nm unpatterned Ag anode. When the anode is patterned with 250 nm nanoholes having a periodicity of 400 nm, strong cavity resonances and higher field intensities within the organic semiconductor layers are observed (Fig. 4(b)). To help distinguish between plasmonic and non-plasmonic effects, the same simulation was performed where the patterned Ag anode was replaced with a patterned Cr anode, a lossy material that does not efficiently support surface plasmons in this wavelength range. The results (Fig. 4(c)) show a slight increase in field when compared to the unpatterned Ag anode; however, the strong plasmonic resonances like those in Fig. 4(b) are not observed. Overall, these FDTD simulations confirm that subwavelength hole arrays in optically thin (12 nm) Ag films are able to produce intense local fields that can enhance the power conversion efficiency of integrated OPVs.

In summary, thin patterned Ag electrodes were fabricated by NSL and used to demonstrate OPV efficiencies that exceed those of devices constructed on a conventional ITO anode. The increase in device performance is attributed to the excitation of surface plasmons and the associated large field enhancements near the anode-donor interface that enhances absorption in the CuPc donor layer. The solutionbased NSL technique allows for processing compatible with low-cost OPV fabrication techniques. This process is also highly tunable, allowing for patterned metallic films of varying hole size and periodicity. Since the NSL technique can be readily extended to massively parallel nanopatterning, it is a promising option to realize low-cost plasmonic photovoltaics using OPVs and other thin-film semiconductors.



FIG. 4. (Color online) Simulated cross-sectional field intensity maps at a wavelength of 622 nm. The anode is varied to demonstrate the difference in plasmonic enhancement for (a) 12 nm unpatterned Ag, and (b) 12 nm patterned Ag having 250 nm hexagonally close-packed holes with a periodicity of 400 nm and (c) a similarly patterned Cr anode.

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