

## Plasmonic excitation of organic double heterostructure solar cells

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The authors demonstrate that thin film organic photovoltaic cells are efficient detectors of surface plasmon polaritons (SPPs). For  $\lambda=532$  nm radiation in a Kretschmann configuration, the external quantum efficiency in fullerene–copper phthalocyanine photovoltaic cells is doubled at resonance to 12%. In thin heterojunction organic photovoltaics, SPP detection relies on a substantial increase in absorption when the incoming radiation is coupled to guided SPPs rather than unguided photons. SPP scattering and nonradiative losses are negligible; however, optical modeling shows that cathode metal penetration into the neighboring organic semiconductor is a major source of loss for SPP or photonic excitation. © 2007 American Institute of Physics. [DOI: 10.1063/1.2714193]

Surface plasmon resonances (SPRs) are commonly used in the real-time detection of chemical and biomolecular interactions at metal interfaces.<sup>1</sup> The main SPR detection methods are based on either the direct measurement of the amplitude or momentum of the reflected optical wave near resonance. Both techniques interrogate the reflected wave using an external photodiode element or array. In this work, we report on an integrated SPR detector using an organic photodetector whose upper electrode composes the active sensing element. Integration offers the benefits of miniaturization and may have wide commercial applications, including industrial process control, environmental testing, point of care diagnostics, and food safety.

To realize SPP detection, we exploit the guided character of surface plasmon polaritons (SPPs). The transduction element is a thin film organic photovoltaic cell.<sup>2</sup> Under conventional illumination, the cell is too thin to absorb much of the incoming radiation. But SPPs propagate parallel rather than perpendicular to device interfaces. The SPP propagation length at  $\lambda=532$  nm is as much as  $\sim 30$   $\mu\text{m}$  for Ag films.<sup>3</sup> This compares to a typical organic photodetector thickness of 0.05  $\mu\text{m}$ . Thus, for absorption limited photodiodes, the propagation distance is a factor of  $<600$  greater than the active device thickness, making absorption more likely.

Photocurrent enhancements in organic Schottky photodiodes under SPP excitation have been previously demonstrated,<sup>4–6</sup> but typical external quantum efficiencies peaked at 0.05%.<sup>5</sup> In this work, we detect the resonant change in total absorption within a thin film organic double heterojunction photodiode, illuminated with  $\lambda=532$  nm excitation in the Kretschmann geometry under attenuated total reflection. The detector is biased in the low-noise photovoltaic (PV) mode. We observe a doubling in external quantum efficiency at SPP resonance compared to the photonic illumination case. The peak external quantum efficiency of 12% represents a factor of 240 improvement in quantum efficiency over previous results. We also present a model of the SPP detector and characterize absorption losses in the metal electrode.

To measure the efficiency of SPP detection, thin film double heterostructure organic photodiodes were fabricated on cleaned glass substrates. Commercially available organic layers were purified by thermal gradient sublimation. Films were deposited at room temperature at high vacuum ( $\sim 10^{-6}$  Torr) in the following order: 235 Å silver, 190 Å of the donor-like copper phthalocyanine (CuPC), and 200 Å of the acceptor-like fullerene ( $\text{C}_{60}$ ). Next, an 85 Å thick layer of bathocuproine (BCP) was grown; BCP has been previously shown to function as an exciton blocking, electron transport layer solar cell.<sup>7</sup> This layer was followed by a 285 Å thick layer of silver shadow masked to define cathodes of area of  $1.4 \times 10^{-2}$   $\text{cm}^2$ .

Light was coupled to the diode via a hemicylindrical prism attached to the glass substrate with index matching fluid; see Fig. 1. The prism and photodiode were mounted on a computer controlled rotating stage and illuminated with  $p$ -polarized light laser of wavelength  $\lambda=532$  nm with an in-

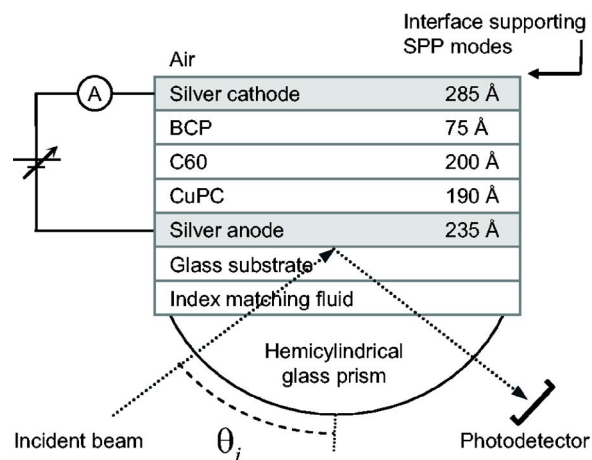


FIG. 1. Monochromatic  $p$ -polarized laser light of wavelength of 532 nm is incident on a prism coupled to the glass substrate through index matching fluid. As  $\theta_i$  increases the onset of total internal reflection precedes an immediate dip in reflected light intensity and increase in monitored photocurrent at SPP resonance. The only interface that can support SPPs in this geometry is at the Ag cathode-air interface. The device structure investigated was glass/Ag (235 Å)/CuPc (190 Å)/ $\text{C}_{60}$  (200 Å)/BCP (75 Å)/Ag (285 Å).

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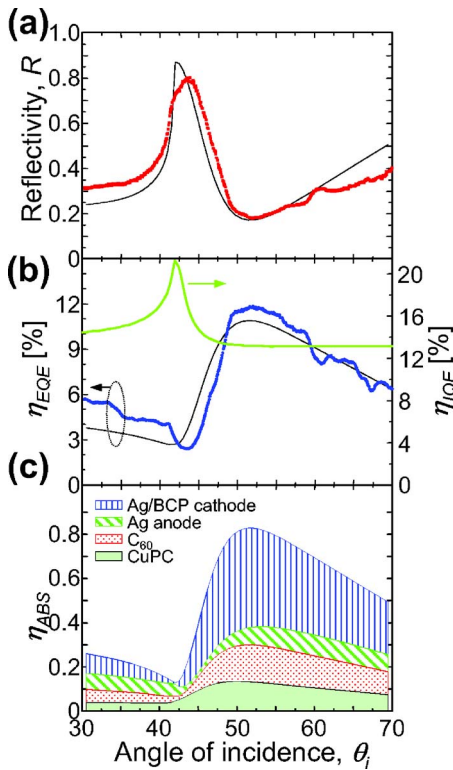


FIG. 2. (Color online) (a) Measured (■) and modeled (solid line) reflectivity spectra sharply increase at  $\theta_i=44^\circ$  corresponding to the onset of total internal reflection from the stack. As  $\theta_i$  increases the reflectivity sharply drops, reaching a minimum at surface plasmon resonance when  $\theta_i=52^\circ$ . (b) The angular positions of maximum and minimum reflectivities align with the measured (●) and modeled (solid line) minimum and maximum external quantum efficiencies. At resonance,  $\eta_{EQE}=12\%$ , reaching twice the efficiency of off resonance excitation at  $\theta_i=30^\circ$ . The modeled internal quantum efficiency decreases slightly under plasmon illumination from 14% to 13%. (c) Modeled optical absorption in all device layers increases by a factor of 3 at resonance.

cident power intensity of  $50 \mu\text{W}$ . The intensity of the reflected beam is monitored with a Si photodetector. The measured photocurrent in air at zero bias is measured with a Keithley sourcemeater. Spectral external quantum efficiency measurements were made by using a xenon lamp with monochromator, chopped at  $\sim 90$  Hz, and measured with a lock-in amplifier. Light intensity was measured with a calibrated silicon photodiode. The indices of refraction and extinction coefficients of all modeled thin films were derived from measurements using an Aquila reflection-transmission thin film spectrophotometer. Because Ag penetrates the thin BCP layer during deposition,<sup>8,9</sup> the optical constants of the cathode were obtained from a BCP/Ag bilayer.

In Fig. 2(a) we plot the reflected light intensity (reflectivity  $R$ ) versus incident illumination angle  $\theta_i$  for  $p$ -polarized incident light. The mixed transverse and longitudinal electromagnetic fields carried by SPPs can only be excited by  $p$ -polarized light and as such, only the  $p$ -polarized reflectivity exhibits a sudden decrease corresponding to SPP excitation at the condition of momentum conservation.<sup>3</sup> As  $\theta_i$  increases, two features are observed: the increase at  $44^\circ$ , which corresponds to the onset of total internal reflection, and a decrease at  $52^\circ$ , which corresponds to destructive interference of backscattered light given the evanescent excitation of a SPP at the Ag cathode-air interface.

In Fig. 2(b), the external quantum efficiency  $\eta_{EQE}$  is plotted versus  $\theta_i$ . The resonance dip in reflectivity correlates

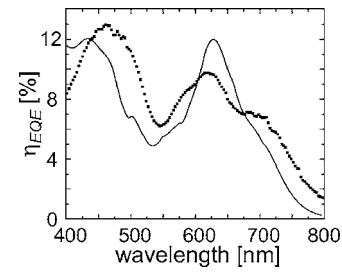


FIG. 3. Measured (■) and modeled (solid line) external quantum efficiency vs wavelength for this device. The angular dependent quantum efficiency was interrogated at  $\lambda=532$  nm, where light absorption occurs nearly equally in  $CuPC$  and  $C_{60}$ .

to a peak in quantum efficiency of 12%, double that at the plane wave illumination.

To estimate the optical absorption within each layer of the SPP detector, we employ the plane wave matrix formalism to calculate the magnitude of the electromagnetic fields throughout the thickness of the device.<sup>10</sup> In Fig. 2(c), we plot the modeled absorption in each layer of the detector. At low angles of incidence,  $\theta_i < \theta_{SPR}$ , photocurrent is primarily limited by low light absorption. For instance, at  $\theta_i=30^\circ$ , the absorption efficiency within the active organic layers,  $CuPC$  and  $C_{60}$ , is  $\eta_{abs}^{org}=10\%$ . At SPR, absorption in the complete stack,  $\eta_{abs}^{total}$ , increases by more than a factor of 3 to 83%, and the absorption within the active layers is  $\eta_{abs}^{org}=30\%$ . The increase in  $\eta_{abs}^{total}$  by a factor of 3 at SPR nearly mirrors the increase in  $\eta_{EQE}$ , confirming that SPP detection is mediated by an increase in absorption. The ratio  $\eta_{abs}^{org}/\eta_{abs}^{total}$  decreases by 2% in resonance, indicating that there is a negligible increase in the fraction of energy lost due to Joule heating and roughness induced scattering under SPP excitation.

To confirm the modeling results,  $\eta_{EQE}$  of this device is plotted in Fig. 3 as a function of wavelength at normal incidence. Below  $\lambda=525$  nm, photocurrent is primarily generated in the  $C_{60}$  layer, while the  $CuPC$  layer primarily absorbs above  $\lambda=525$  nm. At  $\lambda=532$  nm, the extinction coefficients of  $C_{60}$  and  $CuPC$  are approximately equal at  $k=0.10$  and 0.08, respectively, as modeled from the reflectivity-transmission spectra; for derived  $n$  and  $k$ , see supplemental information at EPAPS.<sup>11</sup>

We modeled the BCP/Ag cathode bilayer as a single homogenous film. Seumori *et al.* previously observed deep penetration of evaporation metal on amorphous organic films<sup>8</sup> and Rand *et al.* examined solar cells where Ag penetration into very thin BCP yielded trap states and lowered the barrier to electron extraction.<sup>9</sup> These observations suggest that the BCP cannot be optically modeled as a uniform film, consistent with our findings. We evaporated a bilayer film of BCP and Ag with thicknesses identical to those in the solar cell and measured its absorption spectrum to derive its optical characteristics. The silver penetration into the BCP layer results in a film bilayer that is more absorptive,<sup>11</sup> independent of whether excitation is via SPPs or photons, suggesting that the reduction of metal penetration by alternative electrode deposition methods may increase the internal quantum efficiency in organic PVs.

To model the photocurrent spectrum of Fig. 3, we fit the exciton diffusion lengths by  $L_D^{CuPC}=70 \text{ \AA}$  and  $L_D^{C_{60}}=100 \text{ \AA}$ , similar to previously reported values of  $100 \pm 30 \text{ \AA}$  for  $CuPC$  (Ref. 2) and  $141 \text{ \AA}$  for  $C_{60}$ .<sup>12</sup> The fit is confirmed by com-

parison of the measured and modeled  $R(\theta)$  and  $\eta_{\text{EQE}}(\theta)$  spectra, as plotted in Figs. 2(a) and 2(b). The modeling accurately predicts the angular location and intensity of SPR for both  $R(\theta)$  and  $\eta_{\text{EQE}}(\theta)$  to within  $0.5^\circ$  and 1%, respectively.

Finally, the performance limits of the SPP detector may be assessed from the modeled internal quantum efficiency of the device, defined by the relation  $\eta_{\text{EQE}} = \eta_{\text{ABS}} \cdot \eta_{\text{IQE}}$  and shown in Fig. 2(b).  $\eta_{\text{IQE}}$  incorporates all losses that can occur in photocurrent generation subsequent to light absorption in the stack, including exciton losses during diffusion, and insufficient charge collection. Small deviations in  $\eta_{\text{IQE}}$  are expected near total internal reflection due to spatial modulation of the optical field within the detector, which in turn varies the relative absorption of CuPC and  $C_{60}$ . But the main conclusion is that the organic SPP detector is primarily limited by exciton diffusion losses which yield an internal quantum efficiency of only 13% near resonance. This may be due in part to photo-oxidation of  $C_{60}$ .<sup>7</sup> To increase the sensitivity, the active absorbing layers can be made thinner, which has previously been shown to significantly increase  $\eta_{\text{IQE}}$  by increasing the probability of exciton dissociation at the active interface.<sup>13</sup> In addition, the relative enhancement in detection efficiency compared to the plane wave excitation will also increase. Thus, we expect that higher sensitivities are possible given the device structure optimization.

In summary, we have shown that organic photodiodes excited by surface waves can function as efficient surface plasmon polariton detectors. We have reported a photocurrent increase of  $\sim 200\%$  under resonance, but further optimi-

zation is possible. Approaches include lowering exciton dissociation losses and positioning the active absorbing organic semiconductor closer to the interface supporting surface plasmons polaritons. Finally, we note that excitation by guided waves may offer a general method for enhancing the performance of organic solar cells.

- <sup>1</sup>J. Homola, S. S. Yee, and G. Gauglitz, *Sens. Actuators B* **54**, 3 (1999).
- <sup>2</sup>P. Peumans, A. Yakimov, and S. R. Forrest, *J. Appl. Phys.* **93**, 3693 (2003).
- <sup>3</sup>H. Raether, *Surface Plasmons on Smooth and Rough Surfaces and on Gratings* (Springer, Berlin, 1987), Vol. 111.
- <sup>4</sup>H. Ditlbacher, F. R. Aussenegg, J. R. Krenn, B. Lamprecht, G. Jakopic, and G. Leising, *Appl. Phys. Lett.* **89**, 161101 (2006).
- <sup>5</sup>T. Kume, S. Hayashi, and K. Yamamoto, *Jpn. J. Appl. Phys., Part 1* **32**, 3486 (1993).
- <sup>6</sup>T. Wakamatsu, K. Saito, Y. Sakakibara, and H. Yokoyama, *Jpn. J. Appl. Phys., Part 1* **36**, 155 (1997).
- <sup>7</sup>P. Peumans and S. R. Forrest, *Appl. Phys. Lett.* **79**, 126 (2001).
- <sup>8</sup>K. Suemori, M. Yokoyama, and M. Hiramoto, *J. Appl. Phys.* **99**, 036109 (2006).
- <sup>9</sup>B. P. Rand, J. Li, J. G. Xue, R. J. Holmes, M. E. Thompson, and S. R. Forrest, *Adv. Mater. (Weinheim, Ger.)* **17**, 2714 (2005).
- <sup>10</sup>G. V. Morozov, R. G. Maev, and G. W. F. Drake, *Quantum Electron.* **31**, 767 (2001).
- <sup>11</sup>See EPAPS Document No. E-APPLAB-90-014711 for the indices of refraction and extinction coefficients of CuPC,  $C_{60}$  and BCP/Ag cathode materials used in modeling the device. This document can be reached via a direct link in the online article's HTML reference section or via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>).
- <sup>12</sup>L. A. A. Pettersson, L. S. Roman, and O. Inganäs, *J. Appl. Phys.* **86**, 487 (1999).
- <sup>13</sup>P. Peumans, V. Bulovic, and S. R. Forrest, *Appl. Phys. Lett.* **76**, 2650 (2000).