Interaction of two plasmon modes in the organic photovoltaic devices with patterned back-electrode

D. Lu, E. Rengnath, Y. Cui, Z. Wang, Y. Ding et al.

Citation: Appl. Phys. Lett. 102, 241114 (2013); doi: 10.1063/1.4812242
View online: http://dx.doi.org/10.1063/1.4812242
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v102/i24
Published by the AIP Publishing LLC.

Additional information on Appl. Phys. Lett.
Journal Homepage: http://apl.aip.org/
Journal Information: http://apl.aip.org/about/about_the_journal
Top downloads: http://apl.aip.org/features/most_downloaded
Information for Authors: http://apl.aip.org/authors
Interaction of two plasmon modes in the organic photovoltaic devices with patterned back-electrode

D. Lu,1 E. Rengnath,1 Y. Cui,1 Z. Wang,2 Y. Ding,2 and W. Park1,a)  
1Department of Electrical, Computer and Energy Engineering, University of Colorado, Boulder, Colorado 80309-0425, USA  
2Department of Mechanical Engineering, University of Colorado, Boulder, Colorado 80309-0427, USA

(Received 14 December 2012; accepted 10 June 2013; published online 21 June 2013)

We designed and fabricated silver grating structures on the back-electrodes of organic photovoltaic (OPV) devices to achieve absorption enhancement. The observed enhancement is attributed to several effects, including scattering through corrugated grating surface and surface plasmon modes generated by periodic plasmonic structure. Two plasmon modes are identified in our structure: localized surface plasmon (LSP) and surface plasmon polariton (SPP) modes. The former exists near the absorption edge of the active material and extends the absorption band while the latter provides an absorption pathway in the sub-gap region. Also, LSP is insensitive to active layer thickness and grating period, while the SPP which is excited whenever the momentum matching condition is satisfied shows strong dependence on active layer thickness and grating period. The two modes also exhibit strong interaction as indicated by anti-crossing behavior and thus the interplay between the two modes must be considered for back-electrode design. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4812242]

The photovoltaic (PV) technology moves on to the next-generation devices which typically incorporate thin film active layers as opposed to the bulk silicon technology that has dominated the market for decades. As the active layer thickness becomes comparable to or smaller than the absorption length, the device cannot absorb all incident light and thus light management techniques that can enhance absorption become important. This is especially true for organic PV (OPV) devices in which the active layer thickness must be kept small due to poor diffusion of excitons. There is vast literature on absorption enhancement using various structures among which plasmonic nanostructure is particularly interesting thanks to the strong local field enhancement plasmon structures fabricated on the back-electrode of an OPV device. Two plasmon modes are identified in our structure: localized surface plasmon (LSP) and surface plasmon polariton (SPP) modes. The former exists near the absorption edge of the active material and extends the absorption band while the latter provides an absorption pathway in the sub-gap region. Also, LSP is insensitive to active layer thickness and grating period, while the SPP which is excited whenever the momentum matching condition is satisfied shows strong dependence on active layer thickness and grating period. The two modes also exhibit strong interaction as indicated by anti-crossing behavior and thus the interplay between the two modes must be considered for back-electrode design.© 2013 AIP Publishing LLC.

http://dx.doi.org/10.1063/1.4812242

1D or 2D grating structures in OPV devices. They include embedding plasmonic nanoparticles inside the active layers,2,3 and 1D or 2D grating structures on either the front,4–6 back,7–9 or both surfaces,10 or a combination of both nanoparticles and grating.11 Among these, designing a plasmonic grating structure that could be patterned on the back-electrode is especially attractive as it requires minimal modifications on the conventional device structure. Several groups have investigated organic solar cells with 1D/2D grating on back-electrodes and reported absorption enhancement ranging from 13% to 83%,7–9 which depended on the active layer thickness and other details of the structure. Missing in the literature is the possible presence of multiple modes which may interact with one another. For example, it has been shown that a localized plasmon mode can interact strongly with waveguide modes in a dielectric layer with metallic grating.12 When the OPV with patterned back-electrode supports multiple modes, such an interaction should affect the absorption properties.

In this paper, we investigate the effect of plasmonic grating structures fabricated on the back-electrode of an OPV layer made of a blend (1:2 by weight) of poly[N-900-heptadecanyl-2,7-carbazole-alt-5,5-(40,70-di-2-thienyl-20,10,30-benzothiadiazole)] (P3HT) and phenyl-C61-butyric-acid-methyl-ester (PCBM). P3HT is a relatively recently discovered semiconducting polymer13 with which high-performance organic PV devices have recently been reported.14,15 Similar to many other OPV materials, P3HT has an absorption edge near 660 nm and one of the challenges is to expand the absorption band further into the red and near-infrared region. A simple grating structure can be incorporated on the back-electrode to enhance absorption near the band edge. We performed finite-element modeling using commercial software comsol to design a suitable grating on silver back-electrode. Our discussion is focused on transverse magnetic (TM, E-field perpendicular to grating lines) polarization because the 1D grating structure exhibits plasmon resonances for TM polarization only. Transverse electric (TE, E-field parallel to grating lines) polarization shows almost identical absorbance spectrum except for the absence of the surface plasmon modes. This polarization dependence can be eliminated by using a 2D grating structure but 1D grating under TM polarization offers an adequate model system to study the plasmon mode behaviors. Our simulations showed that one of the effective designs was a

a)Author to whom correspondence should be addressed. Electronic mail: won.park@colorado.edu

References:


We first conducted an extensive numerical modeling study. In this study, experimentally measured dielectric functions for PCDTBT:PCBM, silver and gold were used.\textsuperscript{15,16} In order to separate the absorption by metal from that by the active layer, we used the standard technique of integrating the electromagnetic energy within the active layer volume to estimate the power dissipated within the active layer only.\textsuperscript{17} The absorption by the 30 nm and 60 nm thick PCDTBT:PCBM layers on flat silver film and grating structure are shown in Fig. 1(a). The absorption was increased at all wavelengths when grating structure was introduced but particularly so at wavelengths 650 nm and longer. An interesting observation was that the 60 nm PCDTBT:PCBM on grating exhibited two peaks, while the 30 nm thick sample showed only one peak. To search for the origin of these absorption peaks, we conducted numerical simulations for various thicknesses between 20 nm and 80 nm. Before we get into the details of the different plasmon modes, we first assessed the effect of grating on overall absorption across the entire absorption band by integrating the absorptance spectrum over the visible and near-infrared region where PCDTBT:PCBM has non-negligible absorption. The integrated absorption plotted in Fig. 1(b) represents the fraction of power absorbed by PCDTBT:PCBM when the incident radiation has uniform power spectrum. The total absorption reached a maximum when the thickness was 50 nm and decreased for larger thicknesses despite the larger volume of absorbing material. This behavior was attributed to the interference between the incoming and reflected light in much the same way as typically observed in an anti-reflection coating.\textsuperscript{10} Comparing the same thickness active layers with and without the grating structure, the ones with backside grating had higher absorption in all cases. The absorption enhancement was highest for 20 nm case and decreased down to 11%–12% range for larger thicknesses under TM polarization. For TE polarization, surface plasmon modes were not excited and the absorption spectrum remained almost the same as the flat case. If we take the average of the two polarizations, the enhancement was 10.2% for the 30 nm case and 8.6% for the 60 nm case. The absorption enhancement factor decreasing with increasing active layer thickness is commonly observed. A thinner layer absorbs less and thus offers larger room for enhancement while a thicker layer absorbs more light to begin with and thus tends to show smaller enhancement. However, Fig. 1(b) shows enhancement begins to flatten at 40 nm and actually increases, albeit only slightly, to a maximum value at 60 nm thickness. This unusual behavior is actually related to the two absorption peaks observed for 60 nm sample in Fig. 1(a).

A closer examination of the absorption spectra of PCDTBT:PCBM on grating showed there actually exist two peaks in all thicknesses. Some peaks could not be seen because they were buried inside the intrinsic absorption band of PCDTBT. To circumvent this difficulty, we repeated the same simulations after setting equal to zero the imaginary part of permittivity of PCDTBT:PCBM layer. This eliminated the intrinsic absorption band of PCDTBT while preserving the peak positions of absorption bands due to plasmon modes. The peak wavelengths of the two absorption peaks obtained this way are plotted for various active layer thicknesses in Fig. 2(a) in blue and red dots. Again, the peaks exhibited red shift with increasing active layer thickness resulting in larger effective index. However, the two peaks had very different slopes and showed anti-crossing near the thickness of 30 nm. The peak exhibiting large shift with thickness corresponds to the coupling into the surface plasmon polariton (SPP) mode via grating coupling. To verify this, we numerically calculated the effective index of the SPP mode in the 3-layer system consisting of thick metal substrate, thin dielectric PCDTBT:PCBM film and air for various dielectric layer thicknesses. Once the effective index of the SPP modes was found, it was straightforward to calculate the wavelength that satisfied the grating coupling condition. The grating coupling wavelengths calculated this way are plotted in Fig. 2(a) in blue dashed line with crosses. As

![Graph showing absorption and integrated absorption spectra](image)

FIG. 1. (a) Absorption by the PCDTBT:PCBM layer under TM polarization on flat silver film and the grating structure. The inset shows the schematic of the grating structures with dimensions. (b) Total absorption integrated over the visible to near-infrared region under TM polarization for various thicknesses of PCDTBT:PCBM layer. The difference in total absorption between flat silver film and grating is also plotted on the secondary axis.
shown, the grating coupling wavelengths agreed well with the long wavelength absorption peaks for thicknesses of 40 nm or larger and also with the short wavelength peak at 20 nm thickness. It is thus confirmed that this branch corresponds to the grating coupling into the SPP modes.

The other branch joining the shorter wavelength peaks at thicknesses over 40 nm with the longer wavelength peak of 20 nm thickness showed little changes with increasing active layer thickness. Furthermore, these peaks were found to be largely insensitive to the grating period and incident angle as well (data not shown). For these reasons, it was assigned to be localized surface plasmon (LSP) mode. The nature of these modes is apparent in the field profiles shown in Figs. 2(b)–2(e). Figs. 2(b) and 2(c) show the electric field amplitude at wavelengths of 666 nm and 789 nm, respectively, for the dielectric layer thickness of 80 nm. The LSP mode at 666 nm has the field tightly confined on the sides of the grating line, while the SPP mode at 789 nm exhibits much more spread-out profile of the electric field than the LSP mode. In terms of absorption enhancement, the SPP mode generally showed larger enhancement thanks to the favorable field profile where the field is more stretched out into the absorbing material. Our numerical simulations showed the peak absorption enhancement estimated by the integrated energy density inside the 80 nm thick active material was 9.6× for SPP mode compared with the flat film, while it was 3.2× for LSP. When the two modes mix and exhibit anti-crossing, the field profile changes significantly as shown in Figs. 2(d) and 2(e). As a result of the mixing, the absorption enhancement due to these mixed modes was larger than the LSP mode but smaller than the SPP mode. In the absorption spectra for the 30 nm sample in Fig. 1(a), the two mixed modes were not resolved due to the close proximity and were observed as a single shoulder feature extending the absorption edge. As the active layer thickness was further increased, the SPP and LSP modes became well separated.

Therefore, for the larger thickness samples, the LSP mode extended the absorption edge while the SPP mode produced an additional absorption band in the below-bandgap region. The combined contributions by the LSP and SPP modes resulted in the slight increase in the absorption enhancement factor at thicknesses of over 50 nm shown in Fig. 1(b). This result shows the need to fully understand the presence and interplay between the two different types of plasmon modes to fully optimize the plasmonic grating structure for OPV devices. It is noted that a real OPV device contains additional dielectric layers such as carrier blocking layers and transparent electrode. The presence of additional dielectric layers resulted in shift of surface plasmon mode wavelengths but the absorption enhancement remained mostly unchanged. For a structure consisting of 40 nm ZnO, 120 nm indium tin oxide (ITO), and optically thick glass on top of 80 nm thick active layer, the peak absorption enhancement was found to be 9.4× for SPP mode and 3.4× for LSP mode, respectively.

To experimentally investigate the surface plasmon effects, we fabricated the grating structure by nanoimprint lithography. Briefly, a 200 nm thick silver film was deposited on a plastic substrate. Then, a 170 nm thick poly(methyl methacrylate) (PMMA) was spin-coated and the grating pattern was imprinted using a silicon mold. Any residual PMMA within the trenches was removed by a carefully controlled oxygen reactive ion etching (RIE). To prevent any oxidation of silver during the RIE process, 10 nm thick gold layer was deposited on top of silver before PMMA spin-coating. After imprinting, the PMMA pattern was transferred to silver grating pattern by evaporation of a 20 nm thick silver film and lift-off. As shown in the scanning electron micrograph (SEM) in Fig. 3(a), a highly uniform nanograting structure was obtained over a large area (0.64 cm²).
the surface and grain boundaries. To account for this, we exhibit higher loss due to increased scattering of free electrons by layers on grating. In nanostructures, metals are known to exhibit absorption spectra fitting for grating and PCDTBT:PCBM values given in Ref. The good agreement between the fitting and experimental spectra indicated that the increased imaginary part of the metal permittivity values used in the fitting represented the real structures well. The increased metal loss naturally decreased the absorption by the active layer. While much of the absorption was due to metal, the active layer absorption was nonetheless increased too. From the absorbance spectra of 60 nm thick PCDTBT:PCBM on grating shown in Fig. 3(b), we extracted the active layer absorption enhancement of $1.9\times$. Considering that fabrication imperfections often deteriorate the performance of photonic crystals, the peak enhancement in real devices is expected to be about the same as our case.

In summary, we investigated the effect of metal grating fabricated on the back-electrode of PCDTBT:PCBM OPV structure. Nanopatterned back-electrode offers an effective way to incorporate plasmonic structures for photon management that requires minimal disturbances to the device structure. It was shown that the introduction of back-electrode grating increased absorption by the active layer at all wavelengths in the visible, thanks to the increased light scattering by the corrugated grating surface. Also, the samples with the grating showed additional absorption bands due to the surface plasmon modes. Two different types of surface plasmon modes, SPP and LSP, were identified. The SPP mode presented an absorption band whenever the grating coupling condition was satisfied. An independent computation of the grating coupling condition showed excellent agreement with the observed absorption band positions due to the SPP mode. The LSP mode was found to show only small shift as a function of active layer thickness in contrast to the SPP mode which showed large red shift with increasing thickness. The two type of modes exhibited strong mixing near the thickness of 30 nm, causing significant changes in the mode profiles. The LSP mode, which was relatively insensitive to the active layer thickness, was located at the absorption edge of the active material and thus made a substantial contribution to absorption enhancement for active layer thicknesses of 50 nm or larger while the SPP modes produced additional absorption bands in the below-bandgap region. This study showed the presence and interplay between the two different types of modes in the plasmonic grating patterned on the back-electrode. The full optimization for the energy conversion enhancement for this OPV device, which is currently underway, must take into account the interaction between the multiple modes present in the structure.

Authors gratefully acknowledge Dr. Pierre Verly for providing the ellipsometry data for PCDTBT:PCBM. This work was supported by the National Science Foundation through Grant No. CHE-1125935.

1H. A. Atwater and A. Polman, Nature Mater. 9, 205 (2010).