Suppressing series resistance in organic solar cells by oxygen plasma treatment

Chien-Hung Lin,[1] Shao-Chin Tseng,[2] Yuan-Kui Liu,[2] Yian Tai,[3] Surojit Chattopadhyay,[4] Chi-Feng Lin,[1] Jiun-Haw Lee,[1] Jih-Shang Hwang,[2] Yung-Yu Hsu,[3] Li-Chyong Chen,[5,a)] Wei-Chao Chen,[6] and Kuei-Hsien Chen[6,a)]

[1]*Graduate Institute of Photonics and Optoelectronics and Department of Electrical Engineering, National Taiwan University, Taipei 106, Taiwan*
[2]*Institute of Optoelectronic Sciences, National Taiwan Ocean University, Keelung 20224, Taiwan*
[3]*Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan*
[4]*Institute of Biophotonics Engineering, National Yang-Ming University, Taipei 112, Taiwan*
[5]*Center for Condensed Matter Science, National Taiwan University, Taipei 106, Taiwan*
[6]*Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 106, Taiwan*

We demonstrate a low series resistance contact of gold (anode)/zinc-phthalocyznine in a reverse organic photovoltaic device aided by oxygen plasma treatment. The power conversion efficiency appreciated from 0.2% to 2.13%, post O_2 plasma treatment, predominantly due to the reduction in the series resistance of the device. A depth profile of zinc from x-ray photoelectron spectroscopy study revealed a gold layer with graded zinc composition, instead of pure gold, to be an efficient hole-collector from the organic interface. The zinc alloying of the gold layer has clearly been promoted by the oxygen plasma treatment. © *2008 American Institute of Physics.*
[DOI: 10.1063/1.2940236]

Bilayer and hybrid heterojunction organic photovoltaics (PVs) have recently been intensively investigated for a breakthrough in materials design or process that often limits its performance.[1–5] The electronic properties at the organic/metal interface is a key issue in organic electronic devices. For electron injection into or extraction out of the organic semiconductors, a metal with a suitable work function is preferred as the anode. The cathode side has also been modified by the strategic use of Ca, Mg, or LiF. This technique has previously been used to enhance the electron injection in organic light emitting diodes[6] and the electron extraction in polymer bulk heterojunction solar cells.[7,8] Such modification of the cathode assisted in useful lowering of the work function of cathode material, such as Al.[9] Materials design or selection, interface control,[10] and even postfabrication processing have all shown to improve carrier generation in the active material and collection at both the electrodes.

In this communication, we demonstrate how to improve the contact of Au (anode)/zinc-phthalocyanine (ZnPc) in an Au/ZnPc/n-Si organic/inorganic photovoltaic device by O_2 plasma treatment. This technique can be used routinely to enhance performance in an organic heterojunction PV device. The biggest challenge facing these organic devices is the relatively poor charge extraction at the anode. O_2 plasma treatment will be introduced for this purpose in the organic PV cell processing for performance enhancement. The devices used in this study have been fabricated on n-type silicon wafers having the following structure: Au (10 nm)/ZnPc (60 nm)/n-Si (525 μm)/Al (100 nm). Of these Au, Al, and ZnPc layer were fabricated by evaporation methods. Typically, all the deposition processes were carried out in a multisource chamber at room temperature, a base pressure of 1

$\times 10^{-6}$ Torr and the deposition rate was controlled at 1 Å/s. The active region in our test cell was 0.04 cm^2. A postfabrication with O_2 plasma for 20 min, at power densities of 150 and 250 mW/cm^2 and O_2 pressure of 200 mTorr, was used to modify the Au/ZnPc surface to complete the device. The current-voltage (J-V) characteristics of the solar cells in the dark and illuminated conditions (100 mW cm^{-2} AM 1.5G solar illumination, Thermal Oriel 500W solar simulator) were measured using a Keithley 236 Source-Measure meter. The x-ray photoelectron spectroscopy (XPS) (VG ESCA Scientific Theta Probe using 1486.6 eV Al $K\alpha$ source) measurements were performed on the devices, before and after the O_2 plasma treatments, to study the chemical composition of the device layers. The elemental depth profiling was performed using Ar$^+$ ion sputtering of the device layers at an energy of 0.2 keV.

The optical absorption/transmission spectrum of the individual components of the device is shown in Fig. 1(a). The illumination of the active region can be estimated from the transmission of the top Au layer which is 10 nm thick. The Au layer has a transmittance of $50 \pm 15\%$ in the 400–800 nm spectral region. The incident photon-to-current collection efficiency (IPCE) spectrum of devices, defined as the number of photogenerated carriers per incident photon, with and without the oxygen plasma treatment is shown in Fig. 1(b). The Au transmittance dominates the IPCE spectrum, but the optical responses of the ZnPc or Si are not explicit in it.[11] However, an enhancement in the IPCE with high power oxygen plasma treatment was observed.

A strong increase in photocurrent and fill factor (FF) was observed in the devices upon modification by the O_2 plasma as shown in Fig. 2. The short circuit current density (J_{sc}) was improved from 1.1 to 12.3 mA/cm^2 and the FF from 20.0% to 36.3% resulting in a net gain in the power conversion efficiency (PCE) from 0.21% to 2.1% via the 250 mW/cm^2

a)Authors to whom correspondence should be address. Electronic addresses: chenlc@ntu.edu.tw and chenhk@pub.iams.sinica.edu.tw.
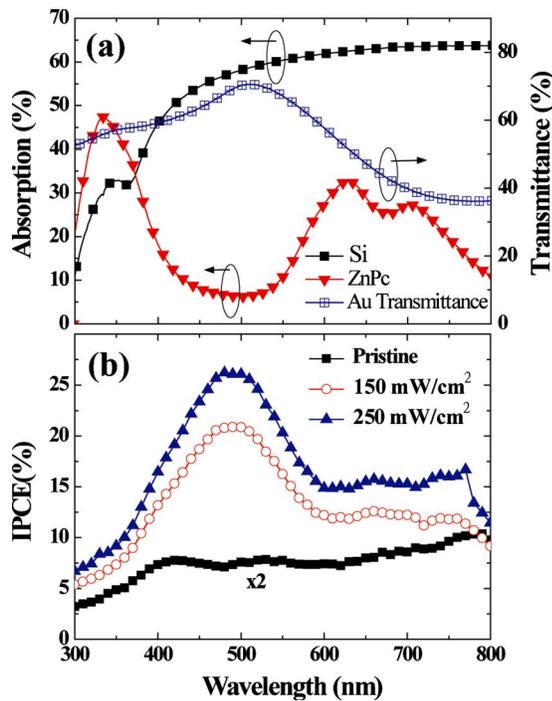
FIG. 1. (Color online) (a) The optical absorption/transmittance of the gold, ZnPc, and silicon layers used in the photovoltaic cell. (b) The IPCE of the device, under short circuit conditions, with and without the oxygen plasma treatments.
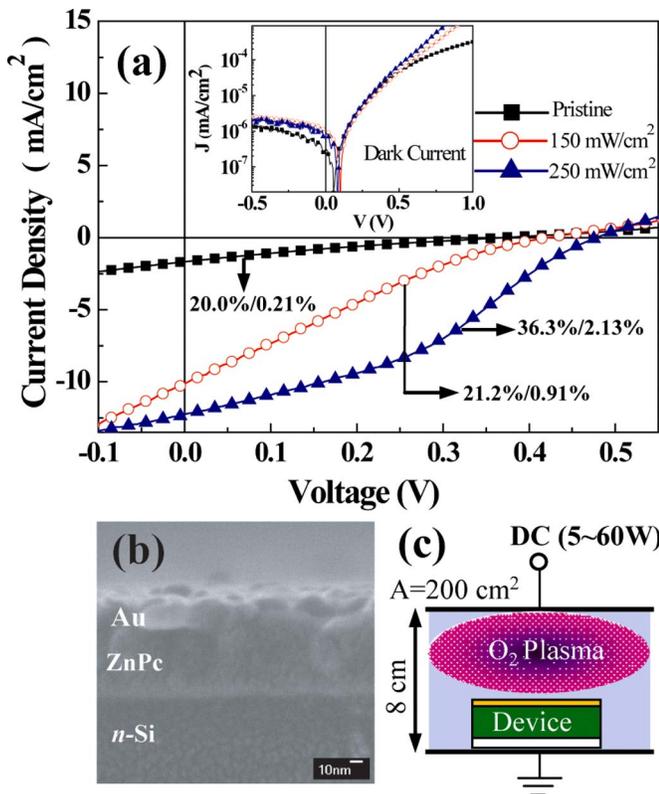

FIG. 2. (Color online) (a) The current density-voltage curve shows the performance of devices with and without oxygen plasma treatment. The numbers associated with each curve designate the FF/PCE (in order) of the particular device. The inset shows the current density-voltage curves under dark conditions. (b) The cross-sectional SEM image of the device structure showing the Si/ZnPc and Au layer thickness. (c) A schematic of the dc plasma system used to generate the O$_2$ plasma.
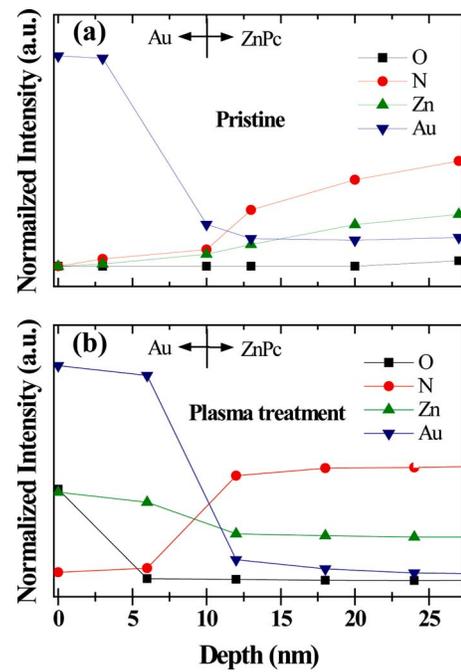

FIG. 3. (Color online) Comparison of the depth profile of oxygen, nitrogen, Zn, and Au distribution from the Au surface to the ZnPc layer measured by XPS on device structures (a) without and (b) with 250 mW/cm^2 O$_2$ plasma treatment.

O$_2$ plasma treatment. The dark current density (inset, Fig. 2), at any given forward bias, is maximum for the 250 mW/cm^2 plasma treated device and minimum for the untreated device. The injection current density improves with the plasma treatment corroborated by the decrease in series resistance from 37.25 Ω, for the untreated device, to 2.35 Ω for the 250 mW/cm^2 plasma treated device. The improvement in the FF for the plasma treated devices could be attributed to this general reduction in the series resistance obtained from the slope of the *J*-*V* curves under $V > V_{OC}$ conditions. Although most of carriers are generated at the *n*-Si/ZnPc interface, their collection is dependent on the contact resistance at the Au/ZnPc interface. In order to understand the suppression in series resistance, a depth profile XPS of the devices was carried out.

A comparison of the elemental depth profile analysis in the untreated and 250 mW/cm^2 plasma treated device is shown in Figs. 3(a) and 3(b), respectively. A strong Au signal without free or bonded Zn contribution was found at the top (depth of 0–10 nm) of the untreated device [Fig. 3(a)]. In comparison, the plasma treated device shows substantial Zn 2$p_{3/2}$ signal in the top Au layer. Nitrogen and Zn, originating from the ZnPc layer, dominate the XPS spectra beyond a depth of 10 nm with feeble signals from O and Au as expected. It was compelling to study why this Zn alloyed Au layer, or an Au layer with Zn impurities, if we may say so, gave better PV performance than the pure Au layer itself in the untreated device.

A careful look at the Zn 2$p_{3/2}$ XPS depth profile spectra of the O$_2$ plasma treated (250 mW/cm^2) device (Fig. 4) revealed the existence of both metallic Zn, Zn^0 at a binding energy of 1021.7 eV, and Zn bonded with nitrogen as in ZnPc, Zn^{2+} at a binding energy of 1022.6 eV. The Au subsurface yielded free metallic Zn signal at 1021.7 eV which shifts to higher binding energies corresponding to Zn–N bonding in ZnPc as we go deeper in the device. The Zn
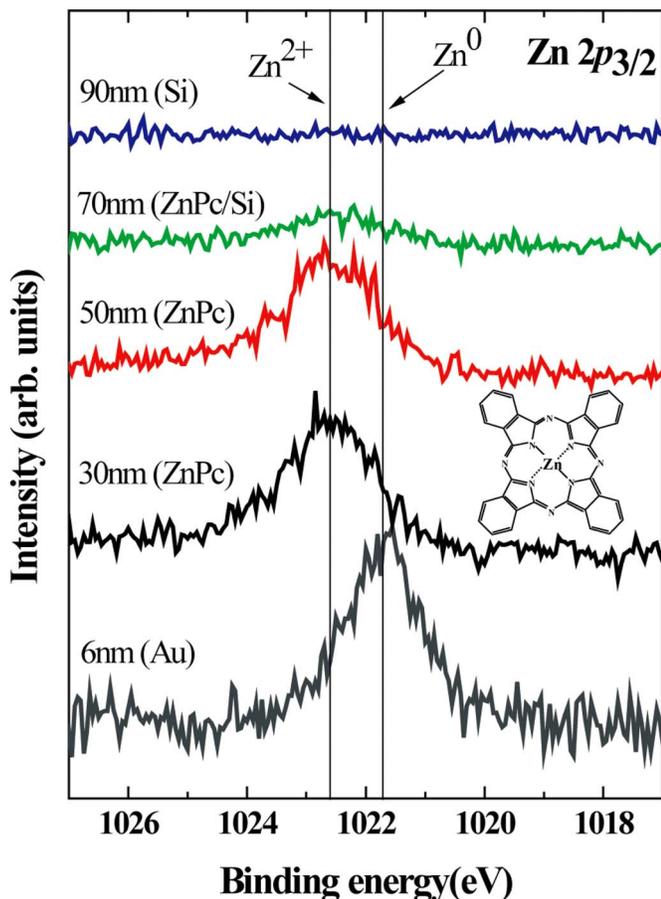
FIG. 4. (Color online) A depth profile of the Zn $2p_{3/2}$ core level XPS spectra of the device after O_2 plasma treatment of 250 mW/cm^2. The plots show the variation of the Zn signal through the top Au layer deep into the silicon substrate.

signal vanishes as we reach the *n*-Si at the bottom of the device. The result suggests a decomposition of the ZnPc near Au interface due to the oxygen plasma treatment and an out diffusion of elemental Zn in the Au layer. The pure Au anode in the untreated device is now replaced with an Au layer, with a graded Zn composition, in the O_2 plasma treated device.

The originally sharp Au/ZnPc interface is electrically weak for the hole extraction[12] and shows a space charge trapping in the organic layer reflected in the poor FF, and higher series resistance at the forward bias. The situation at the Au subsurface changes with the O_2 plasma treatment as free metallic Zn distributes itself within the Au layer with a composition gradient down to the Au–ZnPc interface. This hypothesis is supported by experimental observations of reduced series resistances even by using coevaporated Au and pthalocyanine in the device structure (result not shown). However, coevaporation is inferior to the oxygen plasma treatment since the former results in bulk mixing of Au and ZnPc unlike the controlled interfacial metallic interdiffusion in the latter. Introduction of defect states intermediate to the Au Fermi level (at 5.1 eV) and highest occupied molecular orbital in ZnPc (at 5.28 eV) may provide hopping pathways for the hole towards the anode. This in turn could have modified the absorption of the ZnPc in the 400–600 nm range. The power of O_2 plasma used ensures that the bulk of ZnPc retains the chemical integrity. In conclusion, oxygen plasma treatment was used to reduce the electrical resistance at the anode contact of an organic-inorganic solar cell device that translated into an efficiency gain of about an order in magnitude.

[1] C. W. Tang, Appl. Phys. Lett. **48**, 183 (1986).

[2] P. Peumans and S. R. Forrest, Appl. Phys. Lett. **79**, 126 (2001).

[3] J. Xue, B. P. Rand, S. Uchida, and S. R. Forrest, Adv. Mater. (Weinheim, Ger.) **17**, 66 (2005).

[4] G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, and Y. Yang, Nat. Mater. **4**, 864 (2005).

[5] J. Y. Kim, S. H. Kim, H.-H. Lee, K. Lee, W. Ma, X. Gong, and A. J. Heeger, Adv. Mater. (Weinheim, Ger.) **18**, 572 (2006).

[6] S. E. Shaheen, G. E. Jabbour, M. M. Morrell, Y. Kawabe, B. Kippelen, N. Peyghambarian, M.-F. Nabor, R. Schlaf, E. A. Mash, and N. R. Armstrong, J. Appl. Phys. **84**, 2324 (1998).

[7] C. J. Brabec, S. E. Shaheen, C. Winder, N. S. Sariciftci, and P. Denk, Appl. Phys. Lett. **80**, 1288 (2002).

[8] E. Ahlswede, J. Hanisch, and M. Powalla, Appl. Phys. Lett. **90**, 163504 (2007).

[9] S. Yamaguchi, R. Izaki, K.-I. Yamagiwa, K. Taki, Y. Iwamura, and A. Yamamoto, Appl. Phys. Lett. **83** 5398 (2003).

[10] C. H. Lin, S. Chattopadhyay, C. W. Hsu, M. H. Wu, W. C. Chen, C. T. Wu, S. C. Tsen, J. S. Hwang, J. H. Lee, C. H. Chen, L. C. Chen, and K. H. Chen (unpublished).

[11] H. Tanaka, T. Yasuda, K. Fujita, and T. Tsutsui, Adv. Mater. (Weinheim, Ger.) **18**, 2230 (2006).

[12] W. Chen, L. Wang, D. C. Qi, S. Chen, X. Y. Gao, and A. T. S. Wee, Appl. Phys. Lett. **88**, 184102 (2006).