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Double wavelength ultraviolet light sensitive organic photodetector

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The authors demonstrate an organic ultraviolet (UV) photodetector (PD) device in which 1,3,5-tris(3-methylphenyl-phenylamino)-triphenyamine and 1,3,5-tris(N-phenylbenzimidazol-2-yl)-benzene were used as the electron donor and acceptor, respectively. The PD diode offers responses of 75.2 and 22.5 mA/W as the 365 and 330 nm UV light with 1.0 $\mathrm{mW/cm^2}$ intensities illuminate the PD diode through anode and cathode sides, respectively. It is interesting that only the planar heterojunction structure diode can provide the special response feature while bulk-heterojunction device could not do it. The working mechanism of the PD diode was also discussed in detail. *© 2009 American Institute of Physics*.

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Organic semiconductors, especially the organic photovoltaic (PV) effect based photodetectors (PDs), are regarded as promising candidates in optoelectronic devices due to their unique merits of light weight, low cost, and compatibility with flexible substrates.[1–9] The PV process involves the exciton-generation following photon absorption in donor (D) and acceptor (A) layers, excitons dissociation at D/A interface into free carriers charges which were collected by opposite electrodes. Recently, ultraviolet (UV) PDs have attracted great interest due to their potential applications, such as UV curing monitors, sterilization monitors, etc. Much efforts have been focused on UV-PDs based on inorganic materials such as GaN,[10] SiC,[11] and ZnO,[12] which require complicated manufacturing processes. Thus, organic UV-PDs are considered as a complementary alternative for the inorganic ones. Recently, some organic UV-PDs based on 365 nm UV light have been reported,[13,14] although the UV spectrum covers wavelength range from 190 to 400 nm. In this letter we demonstrate a double wavelength sensitive UV light PD device which can detect either 365 nm or 330 nm light as the two UV lights illuminate the PD through anode and cathode sides, respectively.

It is well known that the performance of organic PD relies on the light absorptions, carrier mobilities and the energy level alignment of donor (D) and acceptor (A) materials. 1,3,5-tris(3-methylphenyl-phenylamino)-triphenyamine (m-MTDATA) is a well-known D-material in exciplex-type light emitting diode[15] due to its lower ionization potential (5.1 eV) and high hole mobility of 3×10^{-5} $\mathrm{cm^2/V\,s}$.[16] Moreover, m-MTDATA shows a maximum absorption at about 350 nm.[17] 1,3,5-tris(N-phenyl-benzimidazol-2-yl)-benzene (TPBi) is a high electron transporting material that presents the maximum absorption locating around 315 nm.[13,18] Thus we consider that if m-MTDATA and TPBi were, respectively, selected as the D- and A-component, a double UV wavelength sensitive PD diode could be demonstrated by skillfully designing the device structure.

All the chemicals were commercially available and various PD diodes with an active area of 2×3 $\mathrm{mm^2}$ were fabricated for device analysis. Organic films and LiF were deposited on patterned indium tin oxide (ITO) glass substrate with a sheet resistance of 25 $\Omega/\square$ by thermal evaporation in a vacuum chamber with a base pressure $<3.0\times10^{-4}$ Pa. After covering patterned metal shadow mask, a 15 nm Al film and a 100 nm Ag film were deposited in turn as the complex cathode. Absorption spectra of the organic films and transmission spectra of the complex cathode were measured with a Shimadzu UV-3101 PC spectrophotometer, respectively. The photocurrent responses (PCRs) of the PD diodes were measured under an illumination of 150 W Xe lamp with a monochromator. Current-voltage (*I-V*) characteristics of the PD diodes were recorded by illuminating with 365 and 330 nm UV light with different intensities through ITO anode and cathode sides, respectively. All the measurements were carried out under ambient condition.

Figure 1(a) depicts the transmission spectra in 200–700 nm wavelength range of several conventional electrode films used in organic electroluminescent diodes. Note that both Al and Mg:Ag films present lower transparence in UV spectra range from 200 to 400 nm, while the transparence at 300–340 nm region of Ag film is higher than those of other electrode films. Figure 1(b) displays the absorption spectra of 30 nm pure films of m-MTDATA, TPBi, and 50 nm 1:1 blend film of m-MTDATA:TPBi on quartz substrates, respectively. It can be seen that maximum absorptions of m-MTDATA and TPBi films lie at about 350 and 315 nm, respectively. Through comparison between Figs. 1(a) and 1(b), it can be seen that the transmission spectrum of Ag film overlaps the absorption spectrum of TPBi film. Taking synthetically consideration of transmission spectra, work functions, and conductivities of all electrode films, Al (15 nm)/Ag (100 nm) film was selected as the complex cathode of the PD diode. The absorption spectrum of the blend film should apparently be a simple superposition of the absorption spectra of the two individual components.

Figure 2(a) describes the PCR spectra of the m-MTDATA/TPBi device under UV light illumination

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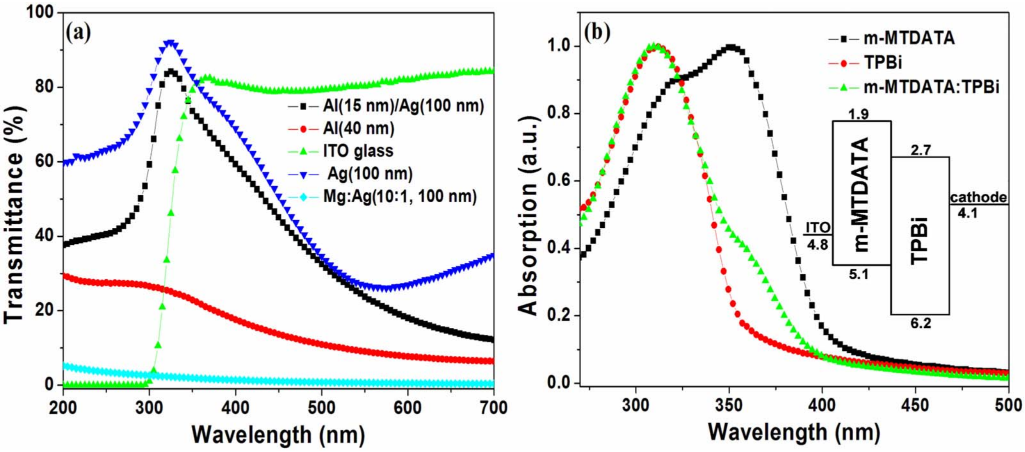

FIG. 1. (Color online) (a) Transmission spectra of several conventional electrode films in 200–700 nm range. (b) Absorption spectra of 30 nm pure films of m-MTDATA, TPBi, and 50 nm 1:1 m-MTDATA:TPBi blend film on quartz substrates. The inset shows the PD diode structure of ITO/m-MTDATA (40 nm)/TPBi (40 nm)/LiF (1 nm)/cathode.

through ITO anode and complex cathode sides, respectively. It is noted that the maximum of PCRs of the former and latter locate at 365 and 330 nm, respectively. The findings would be attributed to weak absorption of TPBi layer for 365 nm and partly to intense absorption of ITO glass substrate for 330 nm light (see Fig. 1). Therefore as a 330 nm light with 1.0 $\mathrm{mW/cm^2}$ was used as the illumination source, the PCR may mainly originate from TPBi absorption. To prove the guess, we fabricated a m-MTDATA:TPBi blend device. When m-MTDATA:TPBi blend device was illuminated by UV light through cathode and ITO glass sides, respectively, the two PCR curves are different from those of the bilayer device, as shown in Fig. 2(b). That is, the two PCR curves are similar and not clearly differentiated like the case of bilayer device. Thus in order to understand the difference of the PCRs between layer-by-layer and blend PD diodes, we carried out two-peak fitting of PCR curve (illuminating through cathode side) of blend PD diode. It is found that the two fitting curves were corresponding with the above-mentioned two PCR curves of bilayer PD device. So we conclude that as the blend PD device works under UV light illumination both TPBi and m-MTDATA molecules play the roles of active components, i.e., the excitons were simultaneously created at the D and A species. But in bilayer-PD diode, m-MTDATA and TPBi layer act as the only active layer under UV light illumination via anode and cathode, respectively.

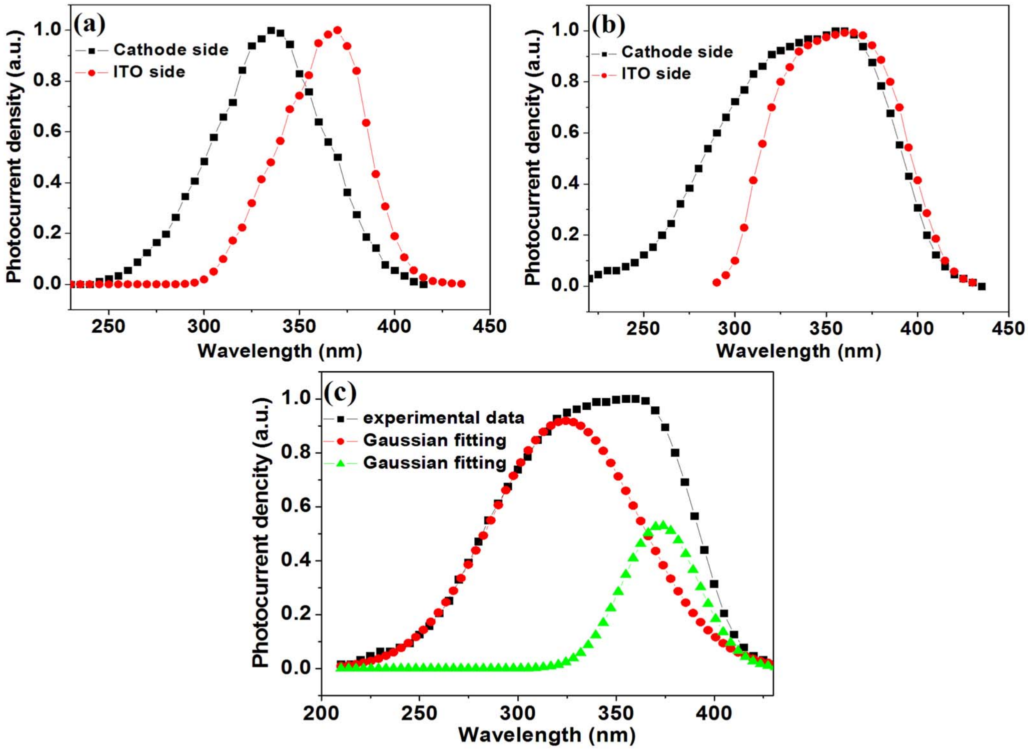

FIG. 2. (Color online) (a) The PCR spectra of the m-MTDATA/TPBi device under illuminations of UV light through ITO anode (circles) and cathode (squares) sides, respectively. (b) The PCR spectra of m-MTDATA:TPBi device under illumination of UV light through ITO anode (circles) and cathode (squares) sides, respectively. The difference between the two curves was attributed to the intense absorption of glass substrate with ITO film at short wavelength range. (c) The Gaussian fitting curves of PCR spectra of the m-MTDATA:TPBi blend device under illuminations of UV light through cathode side.

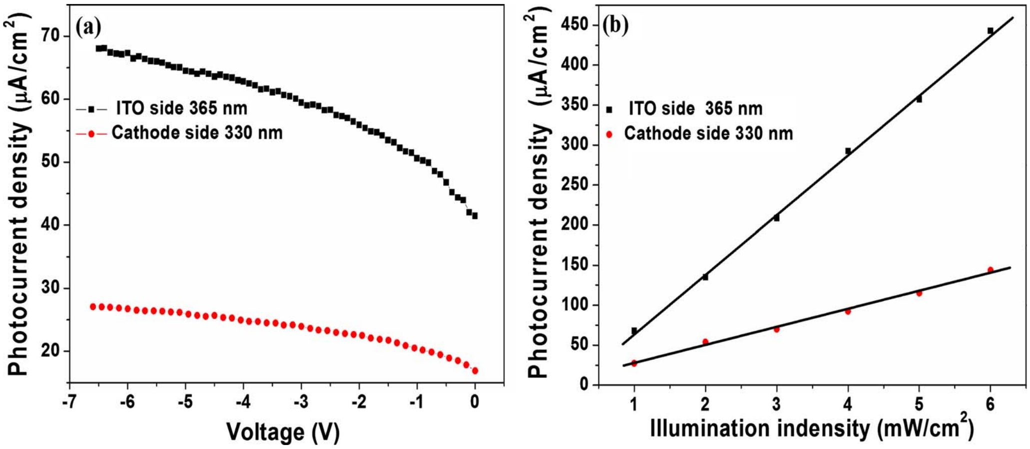

FIG. 3. (Color online) (a) *I-V* characteristics of m-MTDATA/TPBi device at reverse bias under illuminations of 365 nm (squares) and 330 nm (circles) UV lights with an intensity of 1.0 $\mathrm{mW/cm^2}$. (b) Photocurrent density vs illumination intensity of 365 nm (squares) and 330 nm (circles) UV lights, respectively.

Figure 3(a) plots *I-V* characteristics of m-MTDATA/TPBi device at reverse bias under illumination of 365 and 330 nm UV light with an intensity of 1.0 $\mathrm{mW/cm^2}$. When 365 nm UV light illuminates via ITO side, a photocurrent density of 41.5 $\mu\mathrm{A/cm^2}$ at zero bias was measured. The current density increases significantly with the reverse voltage and reaches 68.1 $\mu\mathrm{A/cm^2}$ at −6.5 V, which corresponds to a quantum yield of about 23.2%. By linear fitting, a response of 75.2 mA/W was attained, as shown in Fig. 3(b). When 330 nm UV light illuminates through the cathode side, a photocurrent density of 16.9 $\mu\mathrm{A/cm^2}$ at zero bias was determined, and the current increases significantly with the reverse voltage and reaches 27.1 $\mu\mathrm{A/cm^2}$ at −6.5 V, corresponding to a quantum yield of about 10.2%. By linear fitting, a response of 22.5 mA/W was obtained. Due to the rectifying *I-V* characteristics of the PD device, the dark current of the device is extremely low compared to the photocurrent, i.e., only 0.02 $\mu\mathrm{A/cm^2}$ at −6.5 V.

The working mechanism is understood as following. When 365 and 330 nm UV lights illuminate the PD diode via the anode and cathode sides, respectively, the photons penetrate into the anode and cathode films to enter m-MTDATA and TPBi layers and create excitons. The photogenerated excitons on m-MTDATA and TPBi molecules diffuse to the interface of m-MTDATA/TPBi and a number of free charge carriers were yielded under the built-in electric field.[19] Finally, the charge carriers were collected by anode and cathode, respectively, before the external field was applied. This can be proved by their higher PCR at zero field [see Fig. 3(a)], which differs from that of the D:A blend PD diodes that present less PCR at zero field.[13,14] This would be attributed to the easier transport of the free charge carriers in bilayer structure diode than blend ones.[1] When external field, i.e., the reverse bias voltage, was applied on the diode, the PCR increases with reverse bias because the high-local field at the heterojunction interface favors the dissociation of excitons,[18] and provides an additional force to enhance carriers transport.[1]

In summary, a double wavelength UV light sensitive organic PD diode was demonstrated. The device shows a response of 75.2 and 22.5 mA/W under illuminations of 365 and 330 nm UV light with an intensity of 1.0 $\mathrm{mW/cm^2}$ through anode and cathode sides, respectively. The investigation reveals that the two responses of the double wavelength UV-PD diode were corresponding to the respective absorption of the donor and acceptor components. It could be expected that demonstration of UV-PD diode which is sensitive to shorter wavelength light could present more valuable application anticipation in ultraviolet astronomy, such as solar-blind detection.

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[1] P. Peumans, A. Yakimov, and S. R. Forrest, J. Appl. Phys. **93**, 3693 (2003).
[2] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and J. Heeger, Science **270**, 1789 (1995).
[3] M. Granstrom, K. Petritsch, A. C. Arias, A. Lux, M. R. Andersson, and R. H. Friend, Nature (London) **395**, 257 (1998).
[4] P. Peumans, S. Uchida, and S. R. Forrest, Nature (London) **425**, 158 (2003).
[5] J. Xue, B. P. Rand, S. Uchida, and S. R. Forrest, Adv. Mater. **17**, 66 (2005).
[6] G. Yu, K. Pakbaz, and A. J. Heeger, Appl. Phys. Lett. **64**, 3422 (1994).
[7] L. Ouali, V. V. Krasnikov, U. Stalmach, and G. Hadziioannou, Adv. Mater. **11**, 1515 (1999).
[8] H. W. Lin, S. Y. Ku, H. C. Su, C. W. Huang, Y. T. Lin, K. T. Wong, and C. C. Wu, Adv. Mater. **17**, 2489 (2005).
[9] Y. Kim, M. Ballarotto, D. Park, M. Du, W. Cao, C. H. Lee, W. N. Herman, and D. B. Romero, Appl. Phys. Lett. **91**, 193510 (2007).
[10] J. C. Carrano, P. A. Grudowski, C. J. Eiting, R. D. Dupuis, and J. C. Campbell, Electron. Lett. **33**, 1980 (1997).
[11] P. Sandvik, D. Brown, J. Fedison, K. Matocha, and J. Kretchmer, J. Electrochem. Soc. **152**, G199 (2005).
[12] L. W. Ji, S. M. Peng, Y. K. Su, S. J. Young, C. Z. Wu, and W. B. Cheng, Appl. Phys. Lett. **94**, 203106 (2009).
[13] G. Zhang, W. L. Li, B. Chu, Z. S. Su, D. F. Yang, F. Yan, Y. R. Chen, D. Y. Zhang, L. L. Han, J. B. Wang, H. H. Liu, G. B. Che, Z. Q. Zhang, and Z. Z. Hu, Org. Electron. **10**, 352 (2009).
[14] Z. S. Su, W. L. Li, B. Chu, T. L. Li, J. Z. Zhu, G. Zhang, F. Yan, X. Li, Y. R. Chen, and C. S. Lee, Appl. Phys. Lett. **93**, 103309 (2008).
[15] D. Wang, W. L. Li, B. Chu, Z. S. Su, D. F. Bi, D. Y. Zhang, J. Z. Zhu, F. Yan, Y. R. Chen, and T. Tsuboi, Appl. Phys. Lett. **92**, 053304 (2008).
[16] C. Giebeler, H. Antoniadis, D. D. C. Bradley, and Y. Shirota, Appl. Phys. Lett. **72**, 2448 (1998).
[17] Z. R. Hong, C. S. Lee, S. T. Lee, W. L. Li, and Y. Shirota, Appl. Phys. Lett. **81**, 2878 (2002).
[18] Y. Q. Li, M. K. Fung, Z. Xie, S. T. Lee, L. S. Hung, and J. Shi, Adv. Mater. **14**, 1317 (2002).
[19] J. Nelson, Curr. Opin. Solid State Mater. Sci. **6**, 87 (2002).