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High response deep ultraviolet organic photodetector with spectrum peak focused on 280 nm

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A high response organic deep ultraviolet (DUV) photodetector (PD) with 280 nm as the response spectrum peak was demonstrated. A maximum photoresponse of 309 mA/W under 280 nm UV illumination with an intensity of 0.428 mW/cm^2 and a detectivity of 1×10^{12} $cmHz^{1/2}/W$ at −8 V were achieved, respectively. The optimized PD diode has a structure of ITO/m-MTDATA (10 nm)/m-MTDATA:Bphen(1:1, 60 nm)/Bphen (10 nm)/Cs_2CO_3: Bphen (30 wt %,10 nm)/Al(12 nm)/TPD(40 nm). Under 280 nm constant and shuttered illumination conditions with an intensity of 0.18 mW/cm^2 the operational time is longer than 440 min when its response respectively decreases to 50% and 83% of its original value. The realization of the DUV detection is attributed to the stronger absorption of shorter UV wavelengths of Bphen acceptor and covering UV waveband longer than 300 nm by the TPD layer. The more detailed mechanism of harvesting the high PD performance is also discussed. © *2010 American Institute of Physics*. [doi:10.1063/1.3327833]

Ultraviolet (UV) photodetector (PD) devices which operate in the deep ultraviolet (DUV) region (with peak wavelengths shorter than 300 nm) have attracted much attentions for the development of intrinsic visible-blind PDs for space communications, missile detection, and flame and heat sensing, etc.[1–5] However, most of this kind PDs are inorganic. In this letter we demonstrated an organic DUV PD device using 4,4′,4″-tri-(2-methylphenyl phenylamino) triphenylaine (m-MTDATA) and 4,7-diphenyl-1,10-phenanthroline-(bathophenanthroline) (Bphen) as the donor (D) and acceptor (A), respectively, as well as N,N′-diphenyl-N,N′-bis (3-methyl-phenyl)(1,1′-biphenyl)-4,4′-diamine (TPD) as the spectral defilading layer covering the UV waveband longer than 300 nm. The resulting photocurrent response spectrum peaks at 280 nm and a peak response of 309 mA/W under 280 nm illumination with an intensity of 0.428 mW/cm^2 and a detectivity of 1×10^{12} $cmHz^{1/2}/W$ at −8 V are attained. Besides, the operational lifetime of the DUV PD is about 440 min under a constant illumination of 280 nm UV light with an intensity of 0.18 mW/cm^2 for observing its durability.

All devices were fabricated on cleaned glass substrates precoated with a conducting indium-tin-oxide (ITO) anode with a sheet resistance of 25 Ω/sq and the substrates were treated by UV ozone in a chamber for 15 min after solvent cleaning. The organic films were thermally evaporated in a high vacuum ($<10^{-6}$ Torr) using previously calibrated quartz crystal monitors to determine the deposition rate and the film thickness. The organic layers and semitransparent Al cathode were deposited at a rate of 2 and 10 Å/s respectively. The absorption spectra, transmission spectra, and photoluminescence (PL) spectra of the neat and the blend organic films on quartz substrates were measured with a Shimadzu UV-3101 PC spectrophotometer and a Hitachi F-4500 spectrophotometer, respectively. The current-voltage curves of the devices were recorded in darkness and under the illumination of 280 nm UV light through the Al cathode side. All the measurements were carried out at room temperature under ambient conditions.

Figure 1 depicts the absorption spectra of 30 nm thick neat m-MTDATA, Bphen and their blend film with a 1:1 weight ratio on the quartz substrate, respectively. It is noticed that the absorption of the blend film is mainly corresponding to that of Bphen but the intensity of a shoulder peak at 360 nm is higher than that of Bphen, which is attributed to the stronger absorption band of m-MTDATA component. This indicates that stronger absorption at shorter wavelengths peaked at 280 nm would favor photodetection of deep UV light.

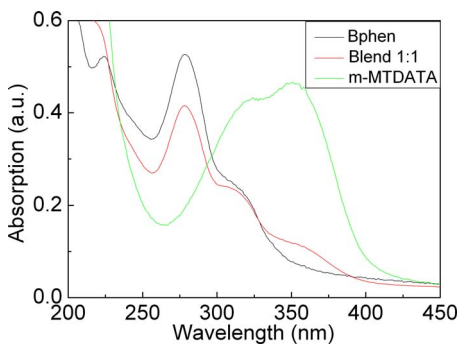

FIG. 1. (Color online) Absorption spectra of 30 nm thick neat m-MTDATA, Bphen, and their blend film with 1:1 weight ratio on quartz substrate, respectively.

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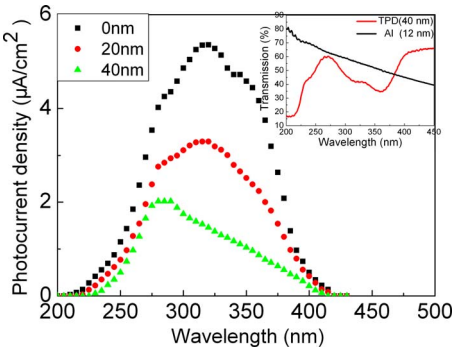

FIG. 2. (Color online) Photocurrent response spectra of the PDs (Device-1, Device-2, and Device-3) with different thickness of TPD film. Inset: the transmission spectra of 40 nm thick TPD and 12 nm thick Al film at 200–450 nm.

First, a series of PD diodes with structures of ITO/m-MTDATA (10 nm)/m-MTDATA:Bphen (1:1, 60 nm)/Bphen (20 nm)/Cs_2CO_3(1 nm)/Al (12 nm)/TPD (x nm) were fabricated. As x is equal to 0, 20, and 40, the devices are referred to device-1, device-2, and device-3, respectively. Figure 2 displays the photocurrent response spectra of the three PD diodes and the inset is the transmission spectra of 40 nm thick TPD and 12 nm thick Al film at 200–450 nm, respectively. We note that all the photocurrent responses are higher at 300–350 nm wavebands and the response peak lies at 320 nm for device-1. In terms of the transmission spectrum of TPD and Al films (inset of Fig. 2), we could deduce that the photocurrent response at 300–350 nm would be decreased thanks to the absorption of TPD film so that a DUV PD diode could be achieved by the enveloping of 40 nm thick TPD film. Finally the photocurrent response peak focuses on 280 nm (device-3).

The photocurrent and dark current densities versus bias voltage of Device-3 under illumination of 280 nm UV light with an intensity of 0.428 mW/cm^2 were measured as shown in Fig. 3(a). We can see that the maximum photocurrent and dark current densities are 110.2 and 0.25 $\mu A/cm^2$ at -8 V, respectively, the former being about 440 times of the latter. A maximum response of 257.5 mA/W is achieved, which is comparable with those of the inorganic DUV-PDs.[6,7] Fig. 3(b) shows photocurrent density versus illumination intensity of 280 nm UV light for Device-3. The photocurrents increase almost linearly with the irradiation intensity of 280 nm UV illumination from 0.02 to 2 mW/cm^2.

To further increase the photoresponse, another device structure is studied and the optimized structure is ITO/m-MTDATA (10 nm)/m-MTDATA:Bphen (1:1, 60 nm)/Bphen(10 nm)/Cs_2CO_3:Bphen (30 wt %, 10 nm) /Al (12 nm)/TPD (40 nm). The response is enhanced to 309 mA/W at -8 V under the same illumination condition for the device-3 keeping unchanged response spectrum. The current ratio of illumination to darkness is about 510 at -8 V. The fact that the photosensitivity increased by the addition of the Cs_2CO_3:Bphen blend layer would be due to balancing charge extraction by the anode and cathode, respectively. This can be understood as follows. Because there is an ohmic contact between m-MTDATA and ITO at the anode side,[8] hole collection should be more efficient. The Cs_2CO_3:Bphen blend layer can produce a *n*-doping effect and increase the electron concentration in the electron-transport layer induced by

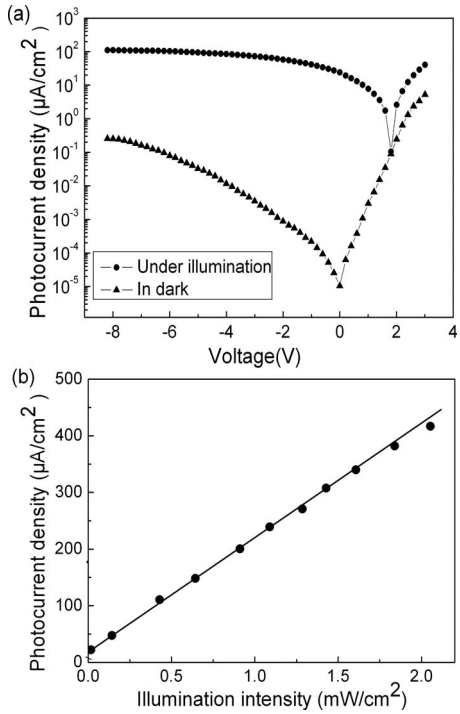

FIG. 3. (a) Photocurrent and dark current densities vs bias voltage for Device-3 under illumination of 280 nm UV light with an intensity of 0.428 mW/cm^2 in logarithm. (b) Photocurrent density vs illumination intensity of 280 nm UV light for Device-3.

Cs_2CO_3 doping.[9] Thus balance between the hole and electron transport toward their respective electrodes would be realized.

In order to roundly characterize the quality of the optimized PD diode its detectivity (D^*) was also calculated. As expected that the shot noise from the dark current is the major contribution to the noise, so the D^* can be expressed as $D^*=R/(2qJ_d)^{1/2}$ (in units of $cmHz^{1/2}/W$), where R is the photoresponse (A/W), q is the absolute value of electron charge (1.6×10^{-19} Coulombs) and J_d is the dark current density (A/cm^2).[10,11] Then we obtained a detectivity of 1×10^{12} $cmHz^{1/2}/W$ at -8 V.

Finally, to assess the degree of degradation caused by photoinduced processes, device stability of the optimized PD devices under constant and shuttered illumination conditions was also observed under 280 nm UV radiation with an intensity of 0.18 mW/cm^2 at -2 V. The latter condition is that at intervals of 5 min the sample is illuminated for 10 s, that is, 3% illumination. The dependences of photocurrent on operating time of the PD diodes are shown in Fig. 4. It can be seen that as the photocurrent falls to 50% and 82% of its initial intensity, the lifetime is 400 min under constant and 3% illumination, respectively. The lifetime parameters of the two measurements indicate that under 280 nm UV illumination with lower radiation intensity the device can work for longer time due to its high detectivity. In other words, to extend the operational lifetime the lower UV illumination dosage is allowed, which can be realized by technologic measure if the response and detectivity of the PD device is sufficiently high.

In conclusion, we demonstrated a peak response of 309 mA/W of a DUV PD diode under 280 nm illumination with an intensity of 0.428 mW/cm^2 and a detectivity of 1×10^{12} $cmHz^{1/2}/W$ at -8 V. The optimized PD diode retains

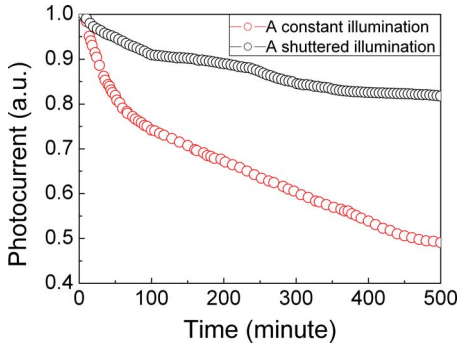

FIG. 4. (Color online) The dependences of photocurrents on operating time for the optimized PD diodes under a constant and shuttered illumination of 280 nm UV light with an intensity of 0.18 mW/cm^2 at -2 V, respectively.

50% and 82% of its original efficiency under constant and shuttered illumination after about 440 min, respectively. The realization of high responsivity for the DUV PD diode is due to stronger absorption of 280 nm UV light of Bphen acceptor, curtaining off the UV light longer than 300 nm by the TPD layer, and balancing carrier transporting toward electrodes. In order to extend the operational lifetime the response and detectivity must be further increased so that the PD diode could work under lower UV illumination dosage.

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