Ultraviolet photodetector with bandpass characteristic based on a blend of PVK and PBD

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We fabricate an ultraviolet photodetector based on a blend of poly (N-vinylcarbazole) (PVK) and 2-tert-butylphenyl-5-biphenyl-1, 3, 4-oxadiazole (PBD) using spin coating. The device exhibites a low dark current density of 2.2×10^{-3} μA/cm^2 at zero bias. The spectral response of the device shows a narrow bandpass characteristic from 300 to 355 nm, and the peak response is 18.6 mA/W located at 334 nm with a bias of –1 V. We also study the performances of photodetectors with different blend layer thicknesses. The largest photocurrent density is obtained with a blend of 90 nm at the same voltage.

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In recent years, semiconductor ultraviolet (UV) photodetectors (PDs) have drawn a great deal of interest due to their various commercial applications in environment monitoring, flame detection, biological and chemical analysis, and so on[1,2]. First, silicon-based inorganic PDs were developed, but they have considerable sensitivity to photons in the visible and infrared spectrum regions in addition to the UV portion of the spectrum. This problem should be addressed through the use of filters. Hence, over the past decade, the effort on UV PDs focused mainly on wide bandgap semiconductors such as III-nitrides[3,4], 4H-SiC[5,6], diamond[7], and II-IV materials[8−10]. However, the qualities of these materials have been difficult to control and the manufacturing process is complicated. Differing from inorganic systems, organic systems are much more attractive for UV PDs as a complementary alternative, with the advantages of low cost, simple to produce, and usable with cheaper or flexional substrates. In the past few years, there have been some demonstrations on organic UV PDs. Ray *et al.* have reported an organic UV PD with a response of 30 mA/W at –15 V based on a blend of N, N'-diphenyl-N, N'-bis (3-methylphenyl)-(1,1′-bi-phenyl)-4, 4′-diamine (TPD) and tris(8-hydroxyquinoline) aluminum (Alq$_3$)[11]. Much work on organic UV PDs has been reported by Li *et al.*; more recently, 4,4′,4″-tris(N-(3-methyl phenyl)-N-phenylamino) diphenylamine (m-MTDATA) has been used as the donor material and various acceptor materials[12−15]. However, these PDs always showed a response with a long wavelength cutoff extending to 400 nm or longer due to the active layers containing at least one material with a relative narrow bandgap smaller than 3.2 eV[12−15]. The active layers of these PDs are also concentrated mainly on the molecular system fabricated by thermal evaporation. PDs based on polymer/molecular systems by spin coating remain scarce.

In this letter, we present an organic UV PDs using material system based on poly (N-vinylcarbazole) (PVK) and 2-tert-butylphenyl-5-biphenyl-1, 3, 4-oxadiazole (PBD) composition by spin coating. The bandgaps of PVK and PBD are 3.6 and 3.8 eV[16], respectively, which result in a shorter cutoff wavelength.

The UV PDs were fabricated on indium tin oxide (ITO)-coated glass substrates with a sheet resistance of 15 Ω/sq. Prior to organic deposition, narrow strips were patterned using wet etching. Next, the substrates were cleaned successively with glass detergent, acetone, ethanol, and deionized water using an ultrasonic bath. Organic bulk heterojunctions were then spin-coated using a solution based on blends of PVK and PBD with a 6:5 weight ratio in chloroform. All solvent and chemical materials were commercially available and used without further purification. Three kinds of PDs using the same solution with different active layer thicknesses were fabricated. The thicknesses of the blend films were 70, 90, and 130 nm, respectively, which were controlled by spin coating rates. After covering a metal shadow mask, a 100-nm-thick Aluminum contact was deposited as cathode by thermal evaporation in a vacuum chamber with a base pressure of 5×10^{-4} Pa. The active area of each device was about 3.6 mm^2.

The organic films for optical measurements were fabricated by spin coating pure or blended films in solution on quartz substrates. UV-visible absorption spectra and transmittance spectra were measured using a spectrophotometer (UV-3101 PC, Shimadzu, Japan). Current-voltage (I-V) characteristics were measured through a source measure unit (2410, Keithely, USA) in the dark and under illumination at 340-nm UV through the ITO glass side. Photocurrent response curves were measured under a xenon lamp coupled to a monochromator. Output power of the monochromatic light was measured with a calibrated Newport830 power meter. All measurements were carried out in ambient air at room temperature.

Figures 1(a), (b), and (c) show the chemical structures of the used materials, schematic structure, and energy level diagrams of the devices, respectively. PVK and

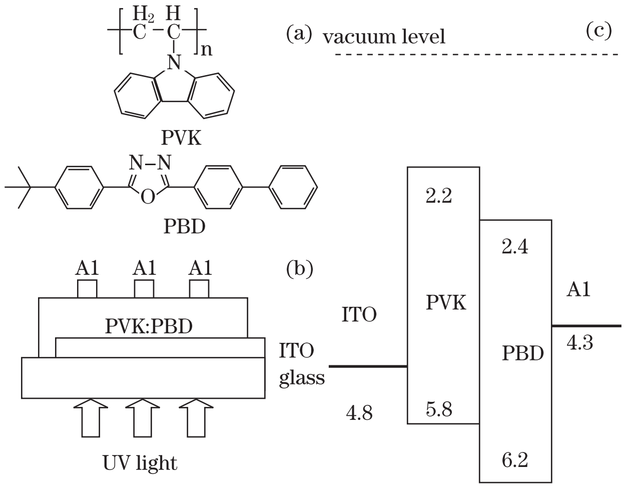

Fig. 1. (a) Chemical structures of PVK and PBD, (b) structure of the device, (c) schematic energy of the device.

PBD were used as donor and acceptor, respectively. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of PVK and PBD were cited from Ref. [16]. Positive voltage was defined as ITO electrode biased positively and all the samples were illuminated through the ITO side.

Figure 2 shows the normalized absorption spectra of PVK, PBD, and their blend film with a 6:5 weight ratio on quartz substrates. The inset is the transmittance spectrum of the ITO glass. As expected, the absorption spectrum of the blend was a superposition of PVK and PBD. The blend film showed a strong absorption in the wavelength shorter than 350 nm, which corresponded to both the wide bandgap of donor and acceptor materials. In comparison, the ITO glass showed an average transmittance more than 75% within the visible region and was not permeable to light with the wavelength shorter than 300 nm.

Figure 3 shows the typical spectrum response of the device at a bias of –1 V. The peak response of the sample was 18.6 mA/W located at 334 nm. The generation of the photoresponse can be explained by the following process. Excitons were created in the active layer under irradiation. Next, the binding electron-hole pairs were separated at the interface of the donor and acceptor materials by transferring an electron (a hole) to acceptor (donor). Finally, photo-generated electrons and holes were driven to the corresponding electrodes under a reverse bias. Therefore, a photocurrent can be detected. Note that the device showed a narrow bandpass characteristic from 300 to 355 nm, which agreed with the absorption spectra and transmittance spectrum in Fig. 2. The short wavelength cutoff was due to the absorption by the glass substrate and the ITO anode electrode, and the long wavelength cutoff corresponded to the wide bandgap of the blend layer. Furthermore, the long wavelength cutoff of the previous reported organic UV PDs was always about 400 nm or longer due to the relative narrow bandgap of the active layer.

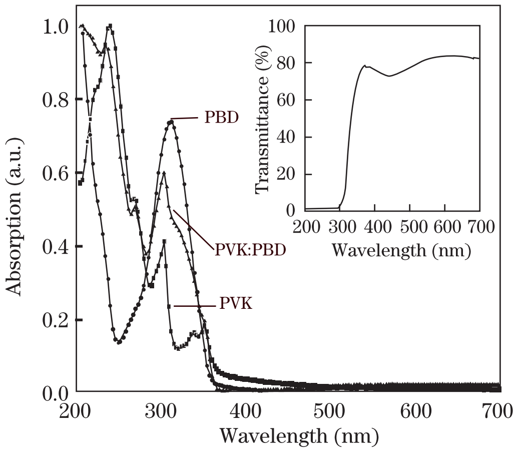

Fig. 2. UV-visible absorption spectra of PVK, PBD and their blend film with 6:5 weight ratio on quartz substrate. Inset: the transmittance spectrum of ITO/glass.

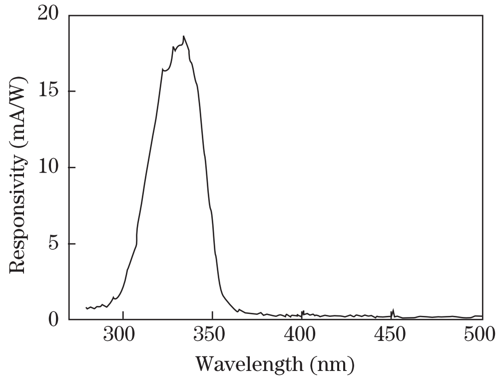

Fig. 3. Spectral response of the photodetector at –1 V.

Figure 4 plots the current density-voltage (J-V) characteristics of the device with a 70-nm active layer in the dark and under illumination of 340-nm UV light with an intensity of 213 μW/cm^2. The inset is a semi-logarithmic plot of the same data. The dark current density at zero bias was $2.2\times10^{-3}\,\mu$A/cm^2, whereas the reverse dark current density remained below $2.5\times10^{-1}\,\mu$A/cm^2 up to a bias of –2 V. The low dark current density helped increase the signal-to-noise ratio (SNR) of the device. The photocurrent density increased as the voltage increased, finally reaching a maximum of 10.2 μA/cm^2 at –2 V.

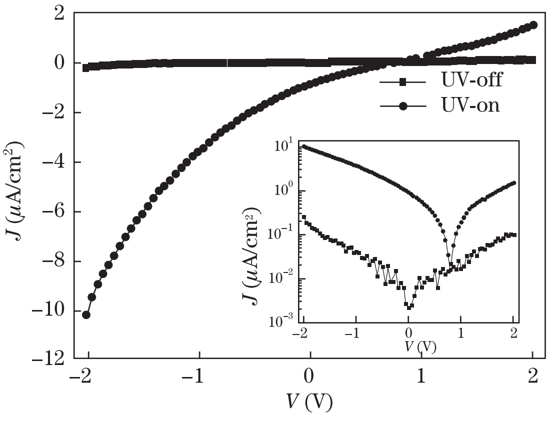

Fig. 4. $J-V$ characteristic curves of the dark current and the photocurrent under illumination of 340-nm UV light with an intensity of 213 μW/cm^2. Semi-logarithmic plot of the same data.

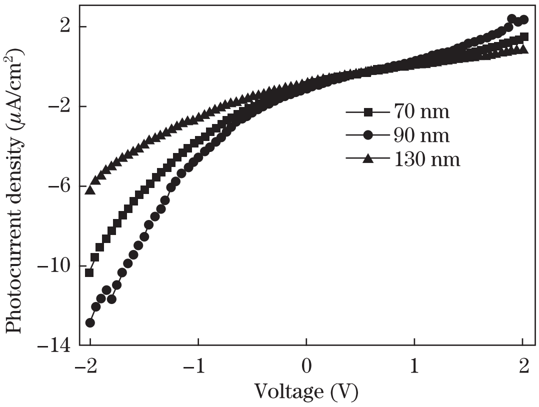

Fig. 5. Photocurrent density as a function of bias for photodetectors with different layer thicknesses.

According to the figure, the device shows an open-circuit voltage (V_{oc}) of 0.8 V, a short-current density (J_{sc}) of 0.9 μA/cm^2, and a fill factor (FF) of 0.21.

To study the effect of organic layer thickness on the performances of the photodetectors, photocurrent densities versus voltage under illumination of 340 nm with different blend thicknesses were measured (Fig. 5). It can be observed that photoresponse has a strong dependence on blend thickness. With the same voltage, the photocurrent densities from large to small correspond to a blend thickness of 90, 70, and 130 nm, respectively. The phenomenon may result from the fact that large thickness conducted a stronger absorption of incident light, so more photo-induced carriers were collected by the electrodes, and the photocurrent densities increased with the thickness increasing from 70 to 90 nm. However, due to the relatively poor carrier transport properties of the PVK and PBD materials[17], further increase in thickness of the blend would be adverse for carriers transporting to their respective electrodes. Thus, the photocurrent densities decreased with a thickness of 130 nm.

In conclusion, organic PDs based on a blend of PVK and PBD are fabricated through spin coating. The spectral response exhibits a bandpass characteristic from 300 to 355 nm, and the peak response is 18.6 mA/W located at 334 nm. Under illumination of 340-nm UV light with the intensity of 213 μW/cm^2, the device shows V_{oc} is 0.8 V, J_{sc} is 0.9 μA/cm^2, and FF is 0.21. The result reveals that the blend of PVK and PBD materials system is a promising alternative for organic UV visible blind photodetectors.

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