Highly-sensitive Broadband Photomultiplication Type All-polymer

Photodetectors and the Applications in Optical Pulse Counting

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Experimental section

Materials

The poly(9,9-bis(3'-(N,N-dimethyl)-N-ethylammoinium-propyl-2,7-fluorene)-alt-

2,7-(9,9-dioctylfluorene))dibromide (PFN-Br) was purchased from Organtec Materials.

Inc. The poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithio

phene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-

c']dithiophene-4,8-dione))] (PBDB-T) was purchased from Solarmer Materials Inc. The PYF-T-O was purchased from eFlexPV Co., Ltd. Lithium fluoride (LiF) was purchased from Jiuyuexincai Technology Co., Ltd. The patterned indium tin oxide (ITO)-coated glass substrates were purchased from South China Science & Technology Co., Ltd. Aurum (Au) was purchased from Zhongnuoxincai Technology Co., Ltd.

Device fabrication

The ITO-patterned glass substrates with sheet resistance of 15 Ω per square were successively washed in detergent, deionized water, and ethanol via ultrasonic cleaning, which were then dried up by high-purity nitrogen gas. The cleaned-up ITO/glass substrates were treated with oxygen plasma for 90 s, aimed for further cleaning and improving work function of ITO. The processed ITO/glass substrates were transferred to a high purity nitrogen-filled glove-box. The PFN-Br was dissolved in methanol to prepared 0.6 mg mL⁻¹ pure solution. PBDB-T was dissolved in chloroform (CF) to prepare 6 mg mL⁻¹ pure solution. PYF-T-O was dissolved in CF to prepare 28, 24, 20 and 16 mg mL⁻¹ pure solutions. The weight ratio of PBDB-T:PYF-T-O in blend solution is 3:100.

The PFN-Br solution was spin-coated onto ITO/glass substrates at the speed of 3000 revolutions per minute (RPM) for 30 s. All the PBDB-T:PYF-T-O blend solutions were immediately spin-coated onto PFN-Br/ITO/glass substrates at the speed of 1000 RPM for 40 s after being stirred on a hotplate of 60 °C for 30 min, which is aimed to prepare active layers with thickness of 140, 160, 180 and 200 nm. 1 nm LiF and 60 nm Au were sequentially thermally evaporated onto active layers in a high vacuum (10⁻⁴ Pa) chamber.

Device characterization

The *J-V* curves of PM-APDs were measured via a Keithley-2400 source meter. The incident monochromatic light was provided by a Xenon lamp coupled with a monochromator. The thickness of films was measured by an AMBIOS technology XP-2 stylus profilometer. The absorption spectra of neat films were obtained by a Shimadzu UV-3101 PC spectrophotometer. The wavelength of incident light was scanned from 300 to 920 nm. The transient photocurrent of PM-APDs was recorded by a Tektronix 5140B oscilloscope under the 850 nm light illumination with intensity of 1 mW cm⁻². The total noise current of PM-APDs was obtained via fast Fourier transform (FFT) for dark current as a function of time.



Fig. S1. Operation principle diagram of PM-APDs.



Fig. S2. Emission spectrum of incident light provided by a Xenon lamp coupled with monochromator.



Fig. S3. (a) R and (b) D* spectra of PM-APDs with different active layer thickness under 4 V bias.



Fig. S4. J-V curves of PM-APDs with LiF layer measured in dark and under white light illumination

with the intensity of 1 mW cm⁻².

 Table S1. R and D* of PM-APDs with LiF layer at 850 nm incident light under 4 V bias.

 Light intensity (uW am²)

 P (A W-1)

 D* (1012 Janas)

Light intensity (µW cm ⁻²)	R (A W ⁻¹)	D* (10 ¹² Jones)
130.42	34.3	2.2
19.13	47.2	3.1
2.81	64.6	4.2
0.42	82.3	5.4
0.06	86.2	5.7



Fig. S5. (a) Photograph and (b) detailed circuit diagram of optical pulse counting based on optimal

PM-APDs.