Hybrid organic/inorganic position-sensitive detectors based on PEDOT:PSS/n-Si

Mohammad Javadi, Mahdiyeh Gholami, Hadis Torbatiyan, and Yaser Abdi

Nanophysics Research Laboratory, Department of Physics, University of Tehran, Tehran 14395-547, Iran

(Received 18 January 2018; accepted 6 March 2018; published online 15 March 2018)

Various configurations like p-n junctions, metal-semiconductor Schottky barriers, and metal-oxide-semiconductor structures have been widely used in position-sensitive detectors. In this report, we propose a PEDOT:PSS/n-Si heterojunction as a hybrid organic/inorganic configuration for position-sensitive detectors. The influence of the thickness of the PEDOT:PSS layer, the wavelength of incident light, and the intensity of illumination on the device performance are investigated. The hybrid PSD exhibits very high sensitivity (>100 mV/mm), excellent nonlinearity (<3%), and a response correlation coefficient (>0.995) with a response time of <4 ms to the inhomogeneous IR illumination. The presented hybrid configuration also benefits from a straightforward low-temperature fabrication process. These advantages of the PEDOT:PSS/n-Si heterojunction are very promising for developing a new class of position-sensitive detectors based on the hybrid organic/inorganic junctions. Published by AIP Publishing. https://doi.org/10.1063/1.5022758

The lateral photovoltaic effect (LPV) arising from nonuniform illumination of a semiconductor junction is the main physical property employed in optical position-sensitive detectors (PSDs).1 PSDs are monolithic large-area optical sensors used for detecting the position of a light spot incident on a surface.2,3 The facility of PSDs for revealing the small displacement of a light spot renders them as attractive optical sensors with various applications in vibration measurements, automated industrial alignment, etc.4 The critical characteristic of the electrical junction utilized for LPV is that the conductivity of one side should be much higher than that of the other side.2,3 In this regard, different configurations have been employed in PSDs including p-n junctions,5,6 metal-semiconductor Schottky junctions,3,7,8 a-Si based configurations,2,4,9 metal-oxide-semiconductor structures,10–13 etc.14–17 In this report, we investigate the LPV of a hybrid organic/inorganic configuration based on the PEDOT:PSS/n-Si heterojunction. PEDOT:PSS [poly(3,4-ethylenedioxythiophene) polystyrene sulfonate] is a transparent p-type conductive polymer with various applications in organic solar cells,18,19 ultraviolet photodetectors,20 and thermoelectric devices.21,22 Hybrid organic/inorganic solar cells based on the PEDOT:PSS/n-Si heterojunction have attracted considerable attention in the past few years.18,19,23,24 The same hybrid junction may be utilized in the optical position sensors which is the topic of this letter. The influence of the thickness of organic layer, the wavelength and intensity of the incident light, and the response dynamics of the PEDOT:PSS/n-Si PSDs are investigated. The hybrid PEDOT:PSS/n-Si exhibits very high LPV sensitivity (>100 mV/mm) and benefits from fast response and recovery dynamics (<4 ms).

Silicon substrates (University, n-type, R < 10 Ω cm, orientation: 100) were initially sonicated in acetone, ethanol, and DI water. PEDOT:PSS solution (OSSILA, PH 1000, R < 0.0012 Ω cm) was spin-coated on the n-Si substrate without any post-treatment and heated at 130 °C for 10 min. This process was then repeated to obtain various thicknesses of the PEDOT:PSS layer on the n-Si substrate. The area of the organic layer in all samples was 1 x 1 cm². For LPV measurements, two Ag contacts (PELCO, Colloidal Silver 16034) were prepared on the both organic and inorganic sides. The distance between the contacts was 4 mm for all samples. In addition, for investigating the optical transmittance of the organic layers, the same process of PEDOT:PSS deposition is repeated on the glass substrates. Morphological investigations, surface topography, and optical transmittance measurements were carried out using an “HITACHI 4160” field emission scanning electron microscope (SEM), an “NT-MDT SOLVER TS-150” atomic force microscope (AFM), and an “AvaSpec Avantes 2048” spectrometer system. For optoelectronic measurements, the samples were mounted on a motorized STANDA positioner. The diameter of the light spots incident on the PSD surface was ~250 μm, and the incident light intensity was recorded using a silicon photodiode (TSL230B; Texas instruments).

Figure 1(a) shows the configuration of the hybrid organic/inorganic PSD utilized for electrical and LPV measurements. Optical transmittance spectra of the PEDOT:PSS layers deposited on glass substrates are presented in Fig. 1(b). The transmittance of the organic layer decreases by increasing the thickness of the layer. Interestingly, the decrement is more notable at the longer wavelengths. While the thinnest PEDOT:PSS layer (220 nm, 1-layer) transmits almost 100% of the incident light at 750 nm, the transmittance of the thickest layer (1720 nm, 6-layer) is less than 50% at the same wavelength. The lower transmittance of the thicker organic layers at longer wavelengths can strongly affect the optical absorption of the hybrid organic/inorganic junction as well as the PSD sensitivity.

Figures 1(c) and 1(d) present the SEM images taken from a typical PEDOT:PSS/n-Si sample. The thickness of the PEDOT:PSS film shown in Fig. 1(d) which is obtained through six cycles of spin-coating/heating processes is around 1720 nm. Figures 1(e), 1(f), and 1(g) present AFM topographic images of the PEDOT:PSS films with 1, 4, and
5 layers, respectively. It is observed that by increasing the number of layers (or the thickness) of the PEDOT:PSS film, the surface roughness as well as the number of small high-z domains increases. Figure 1(h) shows the distribution of surface roughness of the PEDOT:PSS films with various numbers of layers. Comparing the results of Figs. 1(b) and 1(h), it is seen that the lower transmittance of thicker organic layers correlates with their higher surface roughness.

The current-voltage characteristics of the PEDOT:PSS/n-Si heterojunction are presented in Fig. 2(a). The I-V curves are obtained in accordance with the different contacts shown in Fig. 1(a). It is seen that the conductance of the A1-A2 path (i.e. through the organic layer) is almost two orders of magnitude higher than that of the B1-B2 path (i.e. through the silicon). As mentioned above, the critical feature of the junction utilized for LPV is that the conductance of one side should be much higher than that of the other side.1,3 This property of the junction ensures the back-injection process and hence the generation of lateral photovoltage.1–3 In this regard, the hybrid organic/inorganic junction satisfies the critical condition for the LPV effect. The rectifying behavior of the A1-B1 path shows the p-n character of the PEDOT:PSS/n-Si heterojunction (see the inset of Fig. 2(a)). In all of the following results, the A1-A2 path was employed for LPV measurements. Figure 2(b) shows the evolution of current-voltage characteristic of the PEDOT:PSS(1-L)/n-Si under nonuniform IR illumination at different positions between two contacts (λ_{IR} = 810 nm). It is observed that the I-V characteristic is very sensitive to the position of the IR spot. LPV shifts from ~−180 mV to ~+180 mV when the IR spot relocates from −2 mm (contact A1) to +2 mm (contact A2). In addition, a photocurrent (at the zero bias) is also induced due to the inhomogeneous IR illumination. The induced photocurrent varies from ~3.5 μA to ~−3.5 μA as the IR spot moves from −2 mm to +2 mm at the surface of PSD.

Since PEDOT:PSS(1-L) is almost transparent at wavelengths >650 nm [see Fig. 1(b)], the processes of light absorption and photogeneration of excess charge carriers are carried out within the bottom silicon (see the band diagram presented in Fig. 3). Due to the n-type character of substrate silicon and p-type character of PEDOT:PSS,18 the photoexcited electrons remain inside n-Si, while the photoexcited holes are transferred to the organic layer where they can diffuse toward the metallic contacts. The transferred holes are divided between two contacts in regard to the resistance (distance) between the generation site and the metallic contacts.4,17 This process gives rise to a linear variation of LPV with respect to the position of the light spot.

Lateral photovoltage versus the position of IR illumination for various thicknesses of the PEDOT:PSS layer is presented in Fig. 3. It is seen that the LPV decreases by increasing the
thickness of PEDOT:PSS. This decrement is partially due to the lower optical absorption of the bottom silicon owing to the lower transmittance of thicker PEDOT:PSS layers at wavelengths >500 nm [see Fig. 1(b)]. In addition, according to the Monte Carlo simulations,25,26 the lateral (or in-plane) diffusion of charge carriers in a finite thickness layer is inversely related to the thickness of the layer. In this regard, as the thickness of PEDOT:PSS decreases, the in-plane diffusivity of charge carriers increases which assists the higher lateral photovoltage in thinner layers.

The performance of a PSD is characterized by LPV sensitivity, response nonlinearity, and response correlation coefficient.3 Theoretically, LPV is related to the diffusion length of charge carriers in a finite thickness layer is inversely related to the thickness of the layer. In this regard, as the thickness of PEDOT:PSS decreases, the in-plane diffusivity of charge carriers increases which assists the higher lateral photovoltage in thinner layers.

The LPV sensitivity of the hybrid PEDOT:PSS/n-Si junction increases which assists the higher lateral photovoltage in thinner layers.

The performance of a PSD is characterized by LPV sensitivity, response nonlinearity, and response correlation coefficient.3 Theoretically, LPV is related to the diffusion length of charge carriers (Ld), the distance between the contacts (d), and the position of illumination (x) by:

$$LPV = K_m \left\{ \exp\left(\frac{-d/2-x}{L_d}\right) - \exp\left(\frac{-d/2+x}{L_d}\right) \right\}$$

where $K_m$ is a proportional coefficient. The LPV sensitivity is defined as $S = d(LPV)/dx$ which signifies the minimum measurable distance swept by the light spot on the surface of PSD.15,27 The LPV sensitivities of the hybrid PEDOT:PSS/n-Si for various thicknesses of the organic layer are summarized in Table I. LPV sensitivity decreases by increasing the thickness of the PEDOT:PSS layer for the reasons discussed in the previous paragraph. It is noted that the sensitivity of the monolayer PEDOT:PSS/n-Si is almost 106 mV/mm which is among the highest reported values for LPV sensitivity.17,28,29 It is shown that the formation of an inversion layer at the SnSe/Si interface assists the lateral diffusivity of excess carriers resulting in a large LPV.17 Likewise, an inversion layer at the interface of PEDOT:PSS/n-Si junction is formed which facilitates the diffusion of excess hole.30 The formation of the inversion layer can be identified from the nonlinear I-V character of the PEDOT:PSS/n-Si heterojunction in the forward bias (inset of Fig. 2). In this regard, the high LPV of the PEDOT:PSS/n-Si heterojunction originates from the formation of the inversion layer at the interface of PEDOT:PSS/n-Si (see the inset of Fig. 3).

The response nonlinearity is a measure of the output signal distortion of a PSD and is defined as $\delta = 2s/F$ where s and F are the root mean square deviation of the output data from the regression line and the measured full-scale response, respectively.3 Almost for all thicknesses of PEDOT:PSS, the response nonlinearity is less than 3% (Table I) which is favorable when compared to the traditional limit of $\delta \leq 15\%$.3,4 According to Eq. (1), a PSD exhibits small nonlinearity when the condition of $|x| < L_d$ is satisfied.15 In this regard, the small nonlinearity of PEDOT:PSS/n-Si can be attributed to the typically large lateral diffusion length of the photogenerated holes owing to the formation of the inversion layer at the interface of the PEDOT:PSS/n-Si junction (see Table I).

The correlation coefficient (C) shows the linear association of the PSD signal with the position of the light spot.1,4 The value of the correlation coefficient is between zero and one. C = 1 shows a totally positive correlation and C = 0 means no linear correlation. As presented in Table I, the hybrid PSDs exhibit almost totally positive correlation coefficient for all thicknesses of the PEDOT:PSS layer.

The dependence of LPV sensitivity on the wavelength and intensity of the incident light spot is presented in Fig. 4. It is
seen that the sensitivity of the hybrid organic/inorganic PSD increases as the wavelength of the incident light increases. In addition, LPV sensitivity promptly increases by intensifying the incident light spot and then saturates at higher intensities. This observation is consistent with the other Si-based PSDs.\textsuperscript{17,28}

Figure 5 shows the real-time responses of PEDOT:PSS/n-Si to the nonuniform IR illumination incident on the surface of PSD in the vicinity of two metallic contacts. It is seen that, in both regions, the response and recovery characteristic times of the PSD are less than 4 ms which implies the device appropriate response to the nonuniform illumination.

In conclusion, the lateral photovoltage effect in the hybrid PEDOT:PSS/n-Si heterojunction was studied. It is found that the LPV sensitivity for the monolayer PEDOT:PSS spin-coated on the n-Si is almost 106 mV/mm which is among the highest reported sensitivities of the various configurations utilized in PSDs. The LPV sensitivity of the hybrid PSDs decreases by increasing the thickness of the organic layer. Notably, the hybrid PSDs exhibit ideal nonlinearity and response correlation coefficient which remain almost unchanged by the thickness of the PEDOT:PSS layer. The response of the PSD is found to enhance by increasing the wavelength/intensity of the incident light spot. The response and recovery characteristic times of the hybrid PSD are less than 4 ms indicating the device fast response to the inhomogeneous illumination. The advantages of low-temperature and simple fabrication process as well as the exceptional LPV characteristics of the hybrid PEDOT:PSS/n-Si heterojunction are so encouraging for developing a new class of position-sensitive detectors based on the hybrid organic/inorganic junctions.

The authors wish to acknowledge “Iran National Science Foundation (INSF)” and “Iran National Elite Foundation (INEF)” for partial financial support.

\textsuperscript{12}C. Yu and H. Wang, \textit{Adv. Mater.} \textbf{22}(9), 966 (2010).