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# Interface engineering for highly sensitive solution processed organic photodiode

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#### Abstract

We report highly sensitive organic photodiode by introducing a buffer layer between the anode and the semiconductor layer. The effects of buffer layers consisting of a self-assembled monolayer (SAM), PEDOT:PSS, and pentacene on the morphology and crystallinity of the upper-deposited semiconductor layer of a solution-processed small molecule bulk heterojunction are carefully analyzed combined with electrical anlaysis. The active layer is controlled to be nearly homogeneous and to have low crystallinity by using SAM or PEDOT:PSS buffer layers, whereas a highly crystalline morphology is realized by using the pentacene buffer layer. When exposed to light pulses, the external qunatum efficiency and thus the photocurrent are slightly higher for the PEDOT:PSS-based photodiode, however the dark current are lowest for the pentacene-based photodiode. We discuss the origin of the high sensitivity (detectivity of  $1.3 \times 10^{12}$  Jones, linear dynamic range of 95dB) of the pentacene-based photodiode, particularly in terms of the morphology-driven low dark current.

### Keywords

Organic photodiode, Interface engineering, Specific detectivity, Dynamic response, Sensitivity

### **1. Introduction**

Complementary metal-oxide-semiconductor (CMOS) image sensors are rapidly replacing charge-coupled device (CCD) image sensors in imaging applications because of their high resolution and high speeds.<sup>1</sup> The spatial resolution of CMOS image sensors is proportional to the size of a pixel, or to the number of pixels for a given sensor size.<sup>2</sup> Recent technology provided a 1.4 µm pixel size in a 14 megapixel image sensor and even sub-µ pixels is also being investigated.<sup>2,3</sup> Nonetheless, high-end video imaging applications such as ultrahigh definition television require further decreases in pixel size and therefore even higher resolution and higher data rates. However, the detectivity of a photodiode in a pixel decreases rapidly with the size of the photodiode.<sup>4</sup> Although smart device engineering such as backside illuminating technology can provide a partial solution in the form of a small pixel photodiode,<sup>5</sup> the ultimate solution would be to design a new type of photodiode with much higher sensitivity.

One of the major drawbacks of conventional Si photodiodes is that they do not have color selectivity and therefore R/G/B color filters must be inserted, which limits the integrity of the pixels.<sup>6</sup> Organic molecular semiconductors have absorption ranges that can easily be tuned by chemical modification and so are attractive candidates for these applications because they can be stacked in a tandem diode that can sequentially detect R/G/B with a much smaller pixel size. Recently, there have been many successful demonstrations of organic photodiodes with relatively high detectivities.<sup>6-12</sup> Most of these studies have focused either on increasing the photocurrent by adding nanocrystals as sensitizers<sup>7,8</sup> or on decreasing the dark current (and thus the shot noise current) by inserting an electron/hole blocking layer<sup>9,10</sup> in order to enhance the overall detectivity of the organic photodiode. However, there have been few systematic studies of the effects of morphological/structural changes in the organic active layer on the

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performance of the organic photodiode, especially for solution-processed small molecule organic semiconductors.

In this report, we used the well-known small molecule semiconductor,  $^{13}$  7,7' -(4,4-bis(2ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(6-fluoro-4-(5'-hexyl-[2,2'bithiophen]-5-yl)benzo[ c ][1,2,5]thiadiazole), p-DTS(FBTTh<sub>2</sub>)<sub>2</sub>, as a p-type semiconductor and PC<sub>71</sub>BM (PCBM) to fabricate the bulk heterojunction (BHJ) photoactive layer. Three different buffer layers were introduced between the anode and the p-DTS(FBTTh<sub>2</sub>)<sub>2</sub>:PCBM BHJ layers: PEDOT: PSS, a hexamethyldisilazane (HMDS) self-assembled monolayer (SAM), and pentacene. PEDOT: PSS was introduced because it is the hole transport layer (HTL) most widely used in organic photovoltaic devices to smoothen the rough surface of ITO and to align the work functions of ITO and the p-type semiconductor.<sup>14</sup> The SAM was tested because it can be used to tune the interfacial energy level and the morphology of an upperdeposited active laver.<sup>15</sup> Pentacene buffer laver can provide a more favorable interface with the active layer because of their similar surface energies and therefore can minimize the number of charge trapping states at the anode/active layer interface, which is critical to minimizing the transit-time spread of the photodiode. (See the Supporting Information) Furthermore, the photodiode operates in reverse saturation mode, so electron injection from the anode to the active layer can be an important source of dark current, which ultimately limits signal-to-noise ratio. Thus, pentacene can act as a better buffer layer than other materials because of its larger electron injection barrier<sup>16</sup> as well as its lower electron mobility. At the same time, we also need to note that pentacene does absorb in the visible range and therefore will have negative effects on the quantum efficiency and thus the photocurrent. However, if its effects on the dark current and the dynamic behavior of the photodiode outweigh the loss of photocurrent, the insertion of a pentacene buffer layer could still be useful for commercial organic photodiodes. In this study, we found that the pentacene

buffer layer assists the organic photodiode to operate under low dark current. By performing a morphological/structural analysis combined with electrical analysis, we show that the pentacene buffer layer dramatically suppress dark current and thus enabling the conversion of very weak light into photocurrent. As a result, specific detectivities up to  $1.3 \times 10^{12}$  Jones and a linear dynamic range (LDR) up to 95 dB were demonstrated with a solution-processed organic molecular photodiode.

### 2. Results and Discussion

Figure 1(a) shows the diode structure used in this study and (b) shows the absorption spectrum of the p-DTS(FBTTh<sub>2</sub>)<sub>2</sub>:PCBM BHJ. The dark I-V characteristics of photodiodes with various buffer layers (PEDOT:PSS, HMDS SAM, and pentacene) are shown in Figure 1(c). The high dark current of the HMDS diode can be attributed to its very low thickness, which is not sufficient to suppress electron injection from the anode to the BHJ layer in the reverse saturation mode. Other SAMs, such as OTS or ODTS, produced very similar results. The PEDOT:PSS-based diode and the pentacene-based diode exhibit reasonable rectification ratios at  $V=\pm1$  V,  $10^4$  and  $10^5$  respectively. Under the reverse bias, the dark current of these diodes can be attributed to the electron injection from ITO to the active layer and therefore the smaller dark current in the reverse saturation regime in the case of the pentacene-based diode originates partially from the lower conductivity of pentacene and partially from the larger electron injection barrier compared to PEDOT:PSS, as depicted in Figure 1(d).

To further corelate the dark I-V characteristics with morphology of the active layer, we performed atomic force microscopy (AFM) and grazing incident X-ray scattering (GIXS) analyses. Figure 2(a), (b), and (c) show the surface morphologies of the p- $DTS(FBTTh_2)_2$ :PCBM bulk heterojunctions in the presence of the various buffer layers. In the cases of the PEDOT:PSS and HMDS SAM buffer layers, the morphology of the active

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layer is featureless and very smooth with r.m.s. roughness less than 0.5 nm. Incontrast, the pentacene-buffered active layer has an apparently different morphology withlarge terrace-like crystalline domains that are ~ 1  $\mu$ m in size. The 2-D GIXS results shown in Figure 2(d), (e), and (f) support these observations; the crystalline patterns are more developed in the pentacene-based active layer. It is known that the surface energy of the substrate strongly influences the vacuum-deposited pentacene film morphology, resulting in 2-D growth with large dendritic domains at high surface energies and 3-D island growth with small domains at low surface energies.<sup>17</sup> Pentacene was deposited on pristine ITO in this study, so the morphology of the pentacene buffer layer consisted of very large crystalline domains (>1  $\mu$ m, Supporting Information), as is consistent with previous reports of the deposition of pentacene onto surfaces with high surface energies. Furthermore, the surface energy of p-DTS(FBTTh<sub>2</sub>) is closer to that of pentacene rather than PEDOT:PSS as shown in the Fig. S2 of the supporting information. Therefore, it seems that the large crystalline domains of the pentacene buffer layer induce the 2-D growth of the upper-deposited p-DTS(FBTTh<sub>2</sub>)<sub>2</sub> molecules, which generates micron-size terrace-like features.

To further understand the morphology of the active layer on the electrical characteristics, hole-only devices were fabricated and the variations with temperature of their dark I-V characteristics were determined. The representative I-V curves for the hole-only devices are shown in Figure 3(a). The I-V curves follow ohmic behavior at low voltages and closely follow the space charge limited current (SCLC) model at high voltages.<sup>18</sup> Therefore, we can fit the experimental data for the high voltage regime with the well-known Mott-Schottky equation and obtain the charge carrier mobilities. The hole mobility values of the diodes are plotted in Figure 3(b) as functions of temperature within the range 200–300 K. For both the PEDOT:PSS- and pentacene-based diodes, the hole mobilities have Arrhenius-type temperature dependences:

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$$\mu \sim \exp\!\left(\frac{-E_A}{kT}\right)$$

where  $E_A$  is the activation energy, which is closely related to the width of the trap distribution. We can fit the experimental data plotted Figure 3(b) by using the Arrhenius equation and obtain the activation energies. The obtained activation energies for hole transport were 218 meV and 97 meV for the PEDOT:PSS and pentacene buffer layers respectively. The hole-only-device has the same interface between the anode and the semiconductor as the photodiode, so this result implies that the formation of interfacial charge trap states, especially for hole, is suppressed by the pentacene buffer layer. Furthermore, we argue that enlarged crystalline phase of p-DTS(FBTTh<sub>2</sub>) inhibited the percolation pathway for electron through PCBM cluster, resulting in lower dark current. Collectively, these results tell the pentacene buffer layer enabled large crystalline morphology of p-DTS(FBTTh<sub>2</sub>) and in turn enhanced hole injection from ITO to the active layer while suppressing dark current by blocking electron injection from ITO to the active layer.

Figure 4(a) shows the transient responses of the p-DTS(FBTTh<sub>2</sub>)<sub>2</sub>:PCBM photodiodes based on the various buffer layers. When a reverse bias of -0.1 V was applied, all the photodiodes exhibit a dynamic response to light of 650 nm wavelength and 74  $\mu$ W/cm<sup>2</sup> intensity. As expected, the HMDS SAM buffer layer generates a very high dark current. When comparing PEDOT:PSS and pentacene buffer layers, one can see that not only the absolute value of dark current but also its deviation is lower for the pentacene diode than for the PEDOT:PSS diode, which implies that the noise current is also suppressed in pentacene buffered device. Figure 4(b) summarizes the values of the responsivity, which is defined as the generated photocurrent divided by the illuminated light intensity, for these photodiodes under a chopped light pulse of 15 Hz and a wavelength of 650 nm. Despite the dark current and noise level issues the PEDOT:PSS diode exhibits the highest responsivity, over 30 mA/W, because the photocurrent is highest in the PEDOT:PSS diode. Actually, apart from dark current issue, PEDOT:PSS diode resulted in the highest external quantume efficiency over 50% in the range of 500-620 of light wavelength, which is 20% higher than that of pentacene diode as shown in Figure 5. The higher quantum efficiency and thus higher photocurrent in PEDOT:PSS diode can be understood from morphology of the active layer. As described in the section of morphology, p-DTS(FBTTh<sub>2</sub>)<sub>2</sub>:PCBM active layer formed very finely separated morphology on the PEDOT:PSS buffer layer and therefore charge separation could be more efficient compared to the case of the active layer formed on pentacene buffer layer. In other words, one can say that the effect of pentacene buffer layer is actually suppressing dark current by compromising quantum efficiency. When assuming that the shot noise from the dark current is the dominant contribution, the figure of merit of photodiode can be expressed as

# $D^* = R/(2qJ_d)^2$

where *q* is the absolute value of the electron charge  $(1.6 \times 10^{-19} \text{ Coulombs})$ , and  $J_d$  is the dark current density. Under illumination at  $\lambda = 650$  nm with an intensity of 74 µW cm<sup>-2</sup>, PEDOT:PSS and pentacene diodes exhibited D\* of  $1.1 \times 10^{11}$  Jones and  $1.3 \times 10^{12}$  Jones, respectively. Especially, the pentacene diode showed detectivity greater than  $10^{11}$  Jones at almost all the visible range. These results demonstrate that the effect of dark current suppressing by pentacene buffer layer overweight the decrease in quantum efficiency. Therefore, we argue that the morphology control of BHJ films using strategically engineered buffer layer can be an efficient strategy for achieving highly sensitive organic photodiodes. Another important parameter for photodiodes is the linear dynamic range (LDR), which reflects the dynamic range of an photodiode under varying light intensity. LDR is calculated

with the formula<sup>9</sup>

$$LDR = 20\log(j_{\rm ph}^*/j_{\rm d})$$

where  $j_{ph}^{*}$  is the photocurrent measured at a light intensity of 1 mW/cm<sup>2</sup> and  $j_d$  is the dark current. According to this relation, the LDR of the pentacene-based diode is ~ 95 dB, which is close to the best reported values for organic photodetectors and higher than those of other inorganic photodetectors such as InGaAs and GaN.<sup>9,10</sup> A plot of the photocurrent versus the light intensity for our photodiode is shown in Figure 6.

# 3. Conclusion

In summary, we have demonstrated high performance solution-processed small molecule photodetectors. Small molecule semiconductors have the advantage over polymer semiconductors that the absorption edge can be tuned by adjusting their chemical structure, which means they are better candidates for color-selective photodiodes. Solution-deposited organic molecular semiconductors are directly affected by the surface properties of the substrate because of their low molecular weight, so we could control the interface between the anode and the small molecule BHJ layer by inserting various buffer layers. When pentacene was used as the buffer layer, a large terrace-like morphology was generated in the BHJ layer, which was found to suppress electron injection from ITO while enhance hole transport in the active layer compared with the other buffer layers, for which only featureless morphologies were observed. The resulting low dark current of the pentacene photodiode enabled very dynamic photodiode performance. The highest obtained values for the specific detectivity and the LDR were  $1.3 \times 10^{12}$  Jones and 95 dB respectively.

### 4. Experimental Section

General Measurements: UV-Vis absorption spectra were obtained by using a Cary 5000

UV-Vis-near-IR double beam spectrophotometer. Atomic force microscopy (AFM, Multimode IIIa, Digital Instruments) was performed in the tapping mode to obtain surface images of the active layer conjugated to a p-DTS(FBTTh<sub>2</sub>)<sub>2</sub> blend with PC<sub>71</sub>BM on different three buffer layers. All AFM measurements were conducted under ambient conditions. The sample scan area was 5  $\mu$ m × 5  $\mu$ m. 2-D GIXS was performed forstructural analysis at the 3C beamline at the Pohang Accelerator Laboratory (PAL). The measurements were carried out with a sample-to-detector distance of 231.761 mm. Data were typically collected for ten seconds by using an X-ray radiation source of  $\lambda$ = 1.1189 nm with a 2D charge-coupled detector (CCD) (Roper Scientific, Trenton, NJ,USA). The samples were mounted on a homebuilt z-axis goniometer equipped with avacuum chamber. The incidence angle a<sub>i</sub> for the Xray beam was set at 0.17°, which is intermediate between the critical angles of the films and the substrate (a<sub>c,f</sub> and a<sub>c,s</sub>).

Device Fabrication and Characterization: The organic photodiodes were fabricated on prepatterned ITO glass substrates with the structure glass/ITO/buffer layer/p-DTS(FBTTh<sub>2</sub>)<sub>2</sub>:PCBM/LiF/Al (a 0.09 cm<sup>2</sup> active layer). The ITO-coated glass substrates were first cleaned with detergent, deionized water, acetone, and isopropyl alcohol by using ultrasonication. UV/ozone treatment of the cleaned ITO substrates was then performed at room temperature for 30 min. The three different buffer layers (PEDOT:PSS, HMDS SAM, and ITO pentacene) the glass. Poly(3,4were coated onto ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Bay P VP AI 4083, Bayer AG) was spin-coated at 4000 rpm for 60 s with a thickness of 30–40 nm after filtration by using a 0.45 µm PVDF filter. The hexamethyldisilazane (HMDS) SAM layer was spin-coated at 3000 rpm for 30 s by using a 0.3 µm PTFE filter. The coated HMDS SAM layer was then baked in an oven for an hour at 120°C and sonicated in toluene solution for 30 min. The pentacene buffer films were deposited through a shadow mask with organic molecular beam

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deposition (OMBD): deposition rate = 0.1-0.2 Å s<sup>-1</sup>; vacuum pressure ~ $10^{-6}$  Torr; substrate deposition temperature ( $T_{sub}$ ) = room temperature (RT). A blend of p-DTS(FBTTh<sub>2</sub>)<sub>2</sub> and PC<sub>71</sub>BM with a weight ratio of 60:40 was solubilized overnight in chlorobenzene (CB) at a total concentration of 35 mg/mL. The blended solutions were spin-coated at 1750 rpm for 60 s (thickness ~ 70–90 nm) on top of the buffer layer and annealed at various temperatures for 15 min on a hot plate in a glove box. The LiF and Al cathodes were thermally deposited to thicknesses of 0.8 and 100 nm respectively onto the surface of the active layer. The current versus voltage (*J-V*) characteristics of each device without encapsulation were measured in the dark and under an ambient condition AM 1.5G illumination of 100 mV/cm<sup>2</sup> produced by an Oriel 1 kW solar simulator with respect to a PVM 132 reference cell calibrated at the National Renewable Energy Laboratory.

Hole only devices were fabricated with the architecture ITO/PEDOT:PSS or pentacene/ p-DTS(FBTTh<sub>2</sub>)<sub>2</sub>:PC<sub>71</sub>BM / Au. The mobilities were determined by fitting the current density– voltage curves with the Mott–Gurney relationship (space charge limited current).

The current density–voltage (J-V) characteristics were measured using a Keithley 2400 source measure unit under monochromatic illumination from a 150 W Xenon arc lamp assembled with a 1/8 m monochromator. The photocurrent spectra were measured by synchronizing the monochromator with the source meter, a 10 Hz mechanical chopper, and a lock-in amplifier. For low light intensity, the monochromatic light (650nm) was provided by a LED connected to function generator.

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# **Supporting Information**

Surface energy information of the pentacene, PEDOT:PSS and p-DTS(FBTTh<sub>2</sub>)<sub>2</sub> layer. AFM images of pentacene.

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**Figure 1.** (a) Schematic photodiode structure. (b) The UV-vis absorption spectra of pure p-DTS(FBTTh<sub>2</sub>)<sub>2</sub> (filled circles), PCBM (empty circles), and the BHJ (line). (c) The dark I-V characteristics of various photodiodes with buffer layers PEDOT:PSS (squares), HMDS SAM (circles), and pentacene (triangles). (d) The estimated energy levels of the anode and the active layer.



**Figure 2.** Upper panel: AFM images, lower panel: GIXD pattern images. In these panels, the results for the PEDOT:PSS-, HMDS-, and pentacene-based diodes are depicted from left to right.



**Figure 3.** (a) I-V characteristics as functions of temperature ranging 200-300K for both PEDOT:PSS and pentacene based diodes (b) Mobility versus temperature plots to calculate activation energy.





**Figure 4.** (a) Transient responses of the photodiodes with various buffer layers. The insets show enlargements of the data for the dark current areas of the PEDOT:PSS- and pentacenebased diodes on exactly the same scales in the x and y axes. (b) The responsivity versus voltage characteristics of the photodiodes.



**Figure 5.** IPCE (External quantum efficiency) spectra of three different photodiodes based on PEDOT:PSS, pentacene and HMDS buffer layers.







Figure 6. LDR of the pentacene-based photodiode.