A hybrid organic semiconductor/silicon photodiode for efficient ultraviolet photodetection

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Abstract: A method employing conjugated polymer thin film blends is shown to provide a simple and convenient way of greatly enhancing the ultraviolet response of silicon photodetectors. Hybrid organic semiconductor/silicon photodetectors are demonstrated using fluorene copolymers and give a quantum efficiency of 60% at 200 nm. The quantum efficiency is greater than 34% over the entire 200-620 nm range. These devices show promise for use in high sensitivity, low cost UV-visible photodetection and imaging applications.

OCIS codes: (040.7190) Detectors: ultraviolet; (040.6040) Detectors: silicon, (250.3680) Optoelectronics: light emitting polymers; (310.6845) Thin film devices and applications

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1. Introduction

There is a need for convenient photodiodes and multi-pixel detectors with high responsivity across the ultraviolet and visible spectral regions. Such detectors have applications in fields such as spectroscopy [1], nuclear physics [2] and astronomy [3,4]. Ideally these devices should be compatible with existing silicon technology for ease of processing and to be able to take advantage of the wide availability and high spatial resolution of modern silicon CCD detectors.

Silicon photodetectors have very poor responsivity for wavelengths shorter than 400 nm, but increasing responsivity at longer visible wavelengths. Wide bandgap semiconductors do exist for UV detection in the 200-400 nm range such as SiC and GaP [5], as do recently developed evaporated all-organic photodiodes [6–8]. Unfortunately the inorganic devices have no visible sensitivity and the organic devices have narrow spectral responsivity. In addition neither type can be incorporated directly into silicon chips and are difficult to make into multi-pixel imaging devices. As a result, silicon photodetectors with an enhancement layer are widely used for broadband ultraviolet to visible detection [9]. Enhancement layers work by absorbing light at short wavelengths where the silicon photoresponse is poor, and re-emitting it at longer wavelengths, where the photoresponse of silicon is higher.

In order to act as an effective enhancement layer, a material must have high photoluminescence quantum yield (PLQY), broad absorption over ultraviolet wavelengths, and a long emission wavelength to emit photons where silicon detectors have high sensitivity. It should be simple to apply to silicon, and have low self absorption of the emitted light. It should absorb strongly so that a thin film can be used, particularly for imaging applications, as the film needs to be much thinner than the pixel size to avoid blurring of the pixels. Ideally the material should be transparent at visible wavelengths, so as not to degrade longer wavelength performance.

Organic semiconductors have many of these properties: they have strong absorption, high quantum yield in the solid state and can be deposited on a wide range of substrates. Conjugated polymers in particular can be readily spin-coated to make thin films. Previous reports, however, have concentrated on materials deposited by the slower process of evaporation in high vacuum. These have included aluminum tris-8-hydroxyquinoline (Alq3), N,N'-diphenyl-N,N'-bis-(3-methylphenl)-1,1'-biphenyl-4,4'-diamine, and bis-(8-hydroxyquinaldine)-chlorogallium (Gaq2'Cl) [10], lumogen and coronene [4,9,11]. Detector quantum efficiencies of 20-30% and 30-40% have been obtained over the 122 nm – 280 nm wavelength range using lumogen and coronene respectively [11] and evaporated organic coatings are currently widely used for sensitising commercial CCDs [12].

In our study we have focussed on solution-processed materials because they enable simpler fabrication [13] and enable us to easily produce hybrid organic-inorganic semiconductor devices.

2. Photodiode measurements

We started with poly[2,7-(9,9-dioctylfluorene)] (PFO) [14–16], a conjugated polymer shown in Fig. 1, which has good PLQY of $50 \pm 10\%$ in thin films [16]. The PFO was purchased from American Dye Source Inc. (Canada) with part number ADS129BE. This was spin-coated from toluene solution onto fused silica discs and onto a Silonex Inc. (Canada) SLSD-71N5 silicon photodiode. The thickness of the film was determined using a Veeco Instruments (USA) DekTak 150 surface profilometer. The absorption spectrum of the sample on the silica substrate was measured with a Varian Inc. (USA) Cary 300 dual-beam spectrophotometer, and its fluorescence spectrum was measured with a Horiba Jobin-Yvon (USA) Flouromax 2 fluorimeter, giving the results shown in Fig. 2.
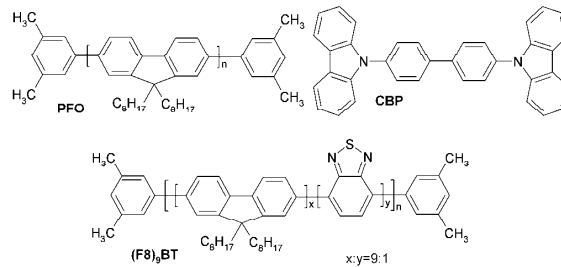

Fig. 1. The molecular structures of poly[2,7-(9,9-dioctylfluorene)] (PFO), 4,4'-N,N'-dicarbazolyl-biphenyl (CBP) and poly(9,9'-dioctylfluorene-co-benzothiadiazole) ((F8)$_9$BT).
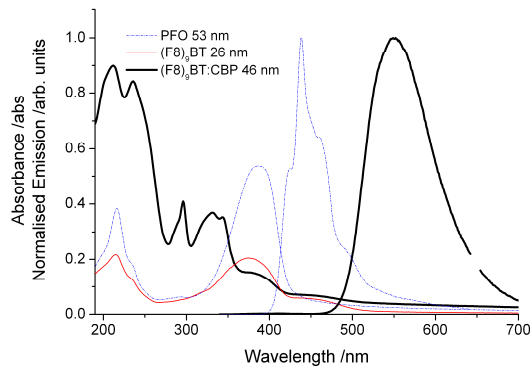

Fig. 2. Absorption and normalised photoluminescence spectra of (F8)$_9$BT:CBP blended 80 wt%/20 wt% films, neat PFO and (F8)$_9$BT films. The thickness of the films used for absorption measurements is given. The photoluminescence spectrum of (F8)$_9$BT neat films were found to be the same as those in the blend (not shown). Photoluminescence spectra were excited at 325 nm.

The photodiode responsivity was measured by using the two beams of the spectrophotometer by comparing the photocurrent from the photodiode to a calibrated Newport Corp. (USA) 818-UV photodetector to determine its spectral responsivity. In turn the spectral response was related to absolute power using a photodiode of known responsivity. The beams were chopped at 30 Hz and the photocurrent was measured using synchronous detection using a pair of Stanford Research Systems (USA) SR830 DSP lock-in amplifiers. The performance of an uncoated Silonex SLSD-71N5 photodiode was also measured. A comparative picture of the measured responsivity and quantum efficiency is reported in Fig. 3, alongside other materials quoted further in this paper.
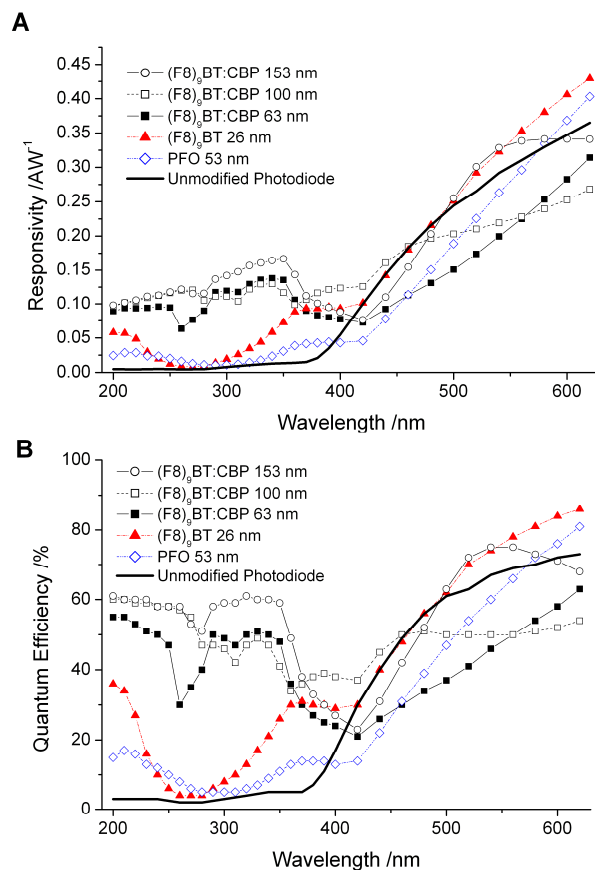
A

B

Fig. 3. Responsivity (fig. a) and quantum efficiency (fig. b) of the unmodified photodiode, and of the photodiodes enhanced with 53 nm PFO, 26 nm of neat $(F8)_9BT$ and 63 nm, 100 nm and 153 nm of 20 wt% $(F8)_9BT$ blended with CBP. Responsivity is shown in terms of photocurrent per unit incident power. Quantum efficiency is defined in terms of electrons of photocurrent per incident photon. All measurements were made at zero bias.

The unmodified photodiode shows very little blue and UV response with less than 6% quantum efficiency and 0.015A/W responsivity below 370 nm. The PFO-coated photodiode shows an enhanced response peaking at 210 nm with 17% quantum efficiency, 0.029 A/W responsivity or 5 times better than the unmodified photodiode. There is also strong enhancement at 390 nm with 14% quantum efficiency, 0.044 A/W responsivity. These peaks appear in the absorption spectrum of PFO. The improvement is modest because the photoluminescence peak of PFO is at 440 nm where the silicon detector still has limited responsivity and there is a large gap in the enhancement in the range 250-350 nm where the PFO has little absorption.

Silicon photodiodes have much higher responsivity at longer wavelength so, to improve the UV efficiency of the hybrid device, we wanted a material with efficient longer wavelength emission, whilst retaining the strong short-wavelength absorption of PFO. Two ways of achieving this are to blend a guest and host material and use energy transfer between them [17], or to use a copolymer containing units with short wavelength absorption capable of transferring energy to a longer wavelength emitter [18]. We chose the latter approach and used a co-polymer containing 90% (9,9-dioctylfluorenyl-2,7-diyl) and 10% (1,4-benzo-{2,1',3}-thiadiazole) units ($(F8)_9BT$) which has an emission peak at 550 nm due to efficient energy transfer to the BT unit [19,20]. This material was obtained from American Dye Source with part number ADS233YE.

Further advantages of this material are that it retains the UV absorption of PFO, the low BT concentration minimises self-absorption of emission, and it has a very high PLQY of 80% [20].

A neat film of (F8)$_9$BT was spin coated from a toluene solution on a photodiode and the resulting responsivity curves are shown in Fig. 3. At 210 nm, the quantum efficiency was 34% and the responsivity 0.057 A/W, 11 times higher than for the unmodified photodiode. At 390 nm the response is increased to 30% quantum efficiency, 0.095 A/W responsivity. The performance is improved in spite of the film used being only 26 nm thick, thus showing the advantage of increasing the separation of the absorption and emission.

A limitation of the above materials is that there is a dip in their absorption spectra in the region of 250-350 nm, leading to a corresponding dip in the photoresponse of the hybrid photodiode. We therefore sought to address this by blending the polymer with a material that complements the (F8)$_9$BT absorption. This requires a material that combines appropriate absorption with appropriate energy levels to transfer energy to the polymer and the ability to produce uniform blends with the polymer. We found that 4,4'-N,N'-dicarbazolyl-biphenyl (CBP) was particularly suitable and, after some optimisation, used a guest-host blend consisting of 80 wt% CBP and 20 wt% (F8)$_9$BT. This gave the desired strong UV absorption, with little absorption at longer wavelengths and strong green emission.

The CBP:(F8)$_9$BT blend's film PLQY was measured in an integrating sphere under nitrogen purge. The sample was excited by the 325 nm line of a He:Cd laser and the light was collected by a calibrated photodiode. The quantum yield was calculated in accordance with the method published by Greenham et al. [21] and found to be 84 ± 10%

The blend was spin-coated onto substrates from a dichloromethane solution. Photodiodes were enhanced with films of thickness 63, 100 and 153 nm, leading to very high quantum efficiencies at 200 nm of 55%, 60% and 61% respectively. These correspond to responsivities of 0.089, 0.097 and 0.098 A/W or enhancement factors of 18-20 times the unmodified photodiode. Notably the dip in the responsivities has now vanished meaning the 153 nm device has >49% quantum efficiency from 200 to 360 nm and the 100 nm device gives >34% quantum efficiency across the entire 200-620 nm range. This exceptional performance was achieved despite the fact that all processing stages and measurements were performed in air. These results imply that solution-coated organic semiconductor enhancement layers could be easily fabricated in air to provide a pathway to simple fabrication of enhanced organic/inorganic hybrid photodetectors.

We note that a report of the use of PFO to enhance photodiode responsivity exists in the patent literature [22]. It does not contain quantitative information about quantum efficiency, but the response of the enhanced device falls by a factor of 100 between 500 nm and 250 nm. In contrast in our blended devices the quantum efficiency is similar at these wavelengths, suggesting that our methodological approach in designing the material structure gives performances two orders of magnitude higher than this early report.

3. Modelling

We have developed a simple model of these hybrid photodiodes, which is similar to the one previously used by Garbuzov [10]. When light is incident on the enhanced photodiode it is either reflected, absorbed by the enhancement layer or passes directly into the silicon detector. Of the light absorbed by the enhancement layer, a fraction of the incident photons (given by the photoluminescence quantum yield) are re-emitted, and a fraction of those reach the silicon photodiode. Any light reaching the silicon detector is converted into a photocurrent by the device's internal quantum efficiency at that wavelength which can be deduced from the unmodified photodiode's reflectivity (not shown) and its responsivity.

Due to the fact the enhancement films are of thicknesses comparable to optical wavelengths they exhibit thin film interference effects which greatly affect their wavelength response. This can be seen in the reflectivity spectra of the enhanced devices shown in Fig. 4

as measured at a 7 degree angle of incidence measured using the absolute reflectivity attachment on the spectrophotometer.
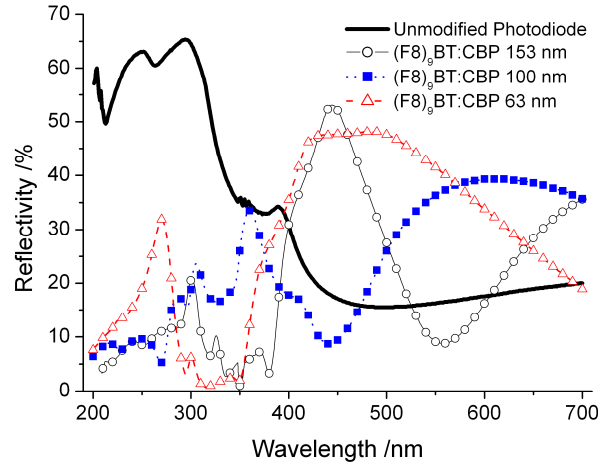

Fig. 4. Reflectivity spectra of the unmodified photodiode, and of the photodiodes enhanced with 63 nm, 100 nm and 153 nm of 20 wt% (F8)$_9$BT blended with CBP.

From the reflectivity and enhancement layer absorption measurements it is possible to calculate the fraction of incident light absorbed by the fluorescent layer (A(λ)) and transmitted into the photodiode (T(λ)) using Eqs. (1) and (2) where R(λ) is the reflectivity, and α(λ) is the absorbance of the enhancement layer.

$$A(\lambda) = (1 - R(\lambda))(1 - 10^{-\alpha(\lambda)}) \tag{1}$$

$$T(\lambda) = (1 - R(\lambda))10^{-\alpha(\lambda)} \tag{2}$$

The fluorescence of the enhancement layer is given by the product of A(λ) and the PLQY, ϕ_{PL}, of the fluorescent material. The fluorescence is trapped by the photodiode according to a coupling efficiency. We assume that fluorescence will be emitted isotropically and escape the device if it is emitted into the solid angle travelling away from the photodiode below the critical angle for total internal reflection [4,10]. It is assumed that light emitted at all other angles will be captured by the detector. Thus the coupling efficiency for fluorescent light into the silicon layers is given by Eq. (3) where n is the refractive index of the enhancement layer and β is the coupling efficiency.

$$\beta = \frac{1}{2}\left(1 + \sqrt{1 - \frac{1}{n^2}}\right) \tag{3}$$

This fluorescence is converted to photocurrent with the photodiode's internal quantum efficiency G(λ). Thus the average detector quantum efficiency for the fluorescent light coupled into the photodiode, Q, is given by the average detector quantum efficiency over the emission spectrum, L(λ), as given in Eq. (4).

$$Q = \frac{\int G(\lambda)L(\lambda)d\lambda}{\int L(\lambda)d\lambda} \tag{4}$$

Therefore the quantum efficiency of the enhanced photodiode, E(λ), is given by Eq. (5).

$$E(\lambda) = A(\lambda)\Phi_{PL}\beta Q + T(\lambda)G(\lambda) \qquad (5)$$

Ellipsometry of CBP films [23] has determined the refractive index at the fluorescence wavelengths to be 1.75. The coupling efficiency β predicted by the total internal reflection capture model is thus 91%.

Using this model with the measured values for ϕ_{PL} and β allows us to obtain curves for the predicted quantum efficiency of the photodiodes, as shown in Fig. 5. These curves show good agreement with the measured photodiode response confirming the validity of this method for estimating the effect of photodiode enhancement layers.
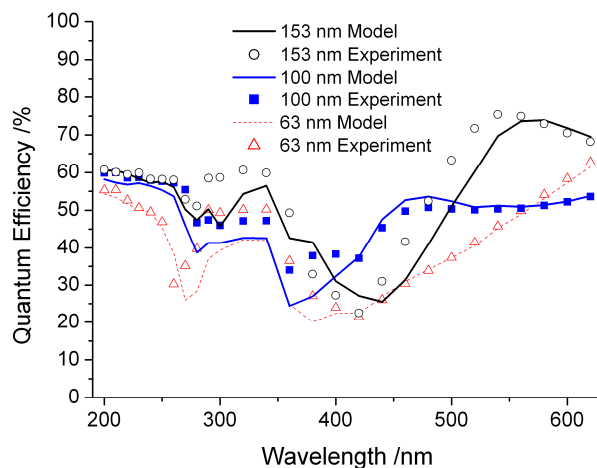

Fig. 5. Predicted and experimental quantum efficiencies of photodiodes enhanced with 63 nm, 100 nm and 153 nm of 20 wt% (F8)$_9$BT blended with CBP. Predicted curves use the experimentally determined values of 84% for the film PLQY and 91% for light coupling efficiency.

4. Conclusions

In conclusion, we have shown that organic semiconductors provide a very simple way of fabricating UV-enhanced organic/inorganic hybrid photodiodes. Our results illustrate the scope to exploit the complementary properties of organic and inorganic semiconductors in hybrid devices. We have studied photodiodes here, and our results complement other work on hybrid lasers [20] and solar cells [24]. Solution processed organic semiconductors offer a wide choice of materials, blend ratios can be easily altered, and layer thicknesses can be chosen by varying spin speed, solvent and solution concentration. This means that absorption, thin film optical properties and emission wavelength can easily be tuned to achieve an optimised photoresponse for the desired wavelength range. We have been able to obtain exceptional UV response (60% EQE at 200 nm wavelength) in a film only 100 nm thick. The use of such a very thin film not only saves material, but minimises pixel crosstalk for potential CCD applications. Accordingly we expect hybrid photodetectors to provide simple to fabricate UV-enhanced photodetectors for both single channel and imaging applications.