All-solution based device engineering of multilayer polymeric photodiodes: Minimizing dark current

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We present photodiodes fabricated with several layers of semiconducting polymers, designed to show low dark current under reverse bias operation. Dark current minimization is achieved through the presence of additional polymer layers that reduce charge carrier injection in reverse bias, when in contact with the device electrodes. All polymer layers are deposited via spin coating and are photocross-linked for allowing further polymer layer deposition, by using a bis-fluorinated phenyl-azide photocross-linking agent. Dark current density values as low as 40 pA/mm² are achieved with a corresponding external quantum efficiency (EQE) of 20% at a reverse bias of ~0.5 V when an electron-blocking layer is used. Dark current is further reduced when both an electron- and a hole-blocking layer are used but the EQE falls significantly. © 2009 American Institute of Physics. [DOI: 10.1063/1.3120547]

Conjugated polymers are attractive materials to use in photodetector arrays that may be patterned by using techniques such as printing. These arrays can be employed in sensor-related applications1–3 and in x-ray medical imaging.4 For obtaining high external quantum efficiencies (EQEs) from these devices, bulk heterojunctions of donor-acceptor blends are used as the active layers for achieving photoinduced charge separation.5–7 Apart from fast response times,3 photodetectors require low dark currents at the operating voltage8 for maximizing their dynamic range. Band structure engineering through the use of multilayer structures is an attractive way to control dark currents in reverse bias, and it has been applied in organic photodetectors based on small molecules.10 Such multilayer structures are difficult to achieve with solution-processed devices due to the difficulty of finding orthogonal solvents for the successive layers.11–13 Multilayer fabrication techniques include lamination,14 inkjet printing,15 and active layer transfer via stamping.16–18

For the bulk heterojunction formed as a (partly demixed) blend of the electron and hole accepting polymers, both materials can be presumed to be present at each carrier-collecting electrode. Such an interpenetrating network of the blend components in the active layer will allow both forward and reverse injection10,19 of electron and hole currents directly into the preferred polymer [Fig. 1(a)]. Carrier injection in the dark can be suppressed to some degree by controlling the electrode work functions19,20 or by the use of suitable blocking layers at the electrodes.18 As Fig. 1(b) shows, these layers provide a barrier to the injection of one carrier in reverse bias while still allowing the passage of the other carrier to the electrode.

Cross-linking techniques have provided useful means for the development of organic optoelectronic devices.21,22 We use here a cross-linking technique23 to fabricate photodiodes of an all-polymer bulk heterojunction layer surrounded by appropriate carrier blocking layers that reduce the dark current. Devices with the optimum layer structure exhibit significant suppression of the dark current density while maintaining relatively high EQEs under realistic reverse bias operating conditions.

FIG. 1. (Color online) (a) A simplified scheme that visualizes the process of dark carrier injection in a photodiode under reverse bias operation. Electron injection (1) takes place from the hole-collecting electrode to the LUMO levels and/or hole injection (2) takes place from the electron-collecting electrode to the HOMO levels of the components of the bulk heterojunction. (b) The effect of blocking layers on the process of charge injection from the electrodes in polymer-based photodiode under reverse bias. Both steps (1) and (2) can be hindered when layers with appropriate frontier orbitals are used as interlayers with electron-blocking (EB) and hole-blocking (HB) properties.

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The materials used for the active layer are poly([9,9-dioctylfluorene]-2,7-diy-[4,7-bis(3-hexylthien-5-yl)-2,1,3-benzothiadiazole]-2,2',-diyl) (F8TBT) and poly(3-hexylthiophene) (P3HT) (regioregularity of 94%). As-spun films with an average thickness of 80 nm were prepared from 1:1 ratio mixtures of these materials in xylene. We have used either P3HT, poly[2,7-(9,9-di-octylfluorene)-co-(1,4-phenylene[4-(sec-butylphenyl)imino]-1,4-phenylene)] (TFB) or poly[9,9’-di-octylfluorenone-co-bis,N’,N’-4-(4-phenylbenzyl)-bis,N,N’-phenyl-1,4-phenyleneimidine] (PFB) as the materials for the electron-blocking (EB) layers. We also have used F8TBT as the material for the hole-blocking (HB) layer. Chemical structures are shown in Fig. 2(a). A Dektek 6M profilometer was used for film thickness determination. The procedure of photodiode fabrication has been described elsewhere. Poly(3,4-ethylenedioxythiophene)-poly(styrene-sulfonate) (PEDOT:PSS) was used as the hole-collecting electrode in these devices. A control device made of 1:1 blend of P3HT:F8TBT (structure A, glass/indium tin oxide (ITO)/PEDOT:PSS/P3HT:F8TBT/Al) was used as a reference. The effect of an intermediate EB layer was studied in structure B (glass/ITO/PEDOT:PSS/P3HT:F8TBT/Al) and structure C (glass/ITO/PEDOT:PSS/PFB/P3HT:F8TBT/Al). Finally, we have investigated the effects of both EB and HB layers in structure D (glass/ITO/PEDOT:PSS/TFB/P3HT:F8TBT/HB/Al) and structure E (glass/ITO/PEDOT:PSS/PFB/P3HT:F8TBT/HB/Al).

The use of water-soluble bis-fluorinated phenyl-azides (FPAs) as cross-linking agents has been described elsewhere. The employed sulfonamide photocross-linking agent [FPA, Fig. 2(a)] is a member of the class of organic-soluble FPAs. Sterically hindered FPAs are capable of cross linking organic polymer semiconductors at lower concentrations without causing significant loss of hole or electron mobility, or of photoluminescence (PL) efficiencies. Rendering the polymer layers insoluble prior to subsequent layer deposition was achieved by adding the cross-linking agent (2 wt %) in the corresponding polymer solution. Spin coating was then performed and the resulting films were exposed to UV irradiation (254 nm) for 5 min. After the exposure to UV light, solvent spin rinsing followed to remove the noncross-linked polymer residues for all structures except device E for which spin rinsing of the second photocross-linked layer was omitted. The thickness of the photocross-linked EB layers was 10–20 nm whereas the thickness of the HB layer was between 10 and 30 nm. The thickness of the as-spun active layers was varied by adjusting the spin-coating speed. The effect of thermal treatment by the annealing of each photocross-linked layer was investigated in device D prior to the subsequent layer deposition. Annealing was performed at ~180 °C for 1 h. For all fabricated devices, annealing was performed at 110 °C for 15 min after the metal cathode deposition. All annealing steps were performed in N2 environment.

Figure 2(b) compares the current density-voltage (J-V) curves of the control blend (device A), the bilayer (devices B and C), and the multilayer (device D) structures. The control device A exhibits high values of dark current density across the whole range of reverse bias voltages being studied. Using P3HT as the EB layer (device B) does not reduce the dark current density of the device; for reverse biases beyond -1 V the dark current density is increased in respect to the control device. Replacing P3HT with PFB (device C) reduces the dark current density in respect to the control. In the low negative voltage regime the dark current density is reduced by approximately an order of magnitude (to 40 pA/mm² at -0.5 V), whereas the reduction is less at more negative voltages (three times reduced at -4 V). Further reduction of the dark current density is observed in multilayer device D. Figure 2(c) focuses with more detail on the effect of the multilayer device arrangements on the dark current density. For device E, we varied the thickness of the active layer. An increase in the device dark current is found as the total film thickness of the device is reduced, consistent with the electric field-driven injection mechanism. For the thickest film the dark current density reduces significantly in respect to the control device of Fig. 2(b). The need for rendering the photocative middle layer insoluble prior to the deposition of the HB layer is also manifested in Fig. 2(c). Without cross linking of the active layer, partial removal and subsequent thickness reduction of this layer occur during HB deposition, and the dark current density is at least one order of magnitude higher.

Figure 3 presents the EQEs of the photodiodes under a range of reverse bias conditions. We note that the onset for photocurrent near 650 nm matches the absorption for P3HT and F8TBT. For all cases, in respect to their short circuit mode, the photodiodes exhibit improved EQEs when operated under reverse bias. We attribute this observation to the effects of field-assisted separation and collection of the photogenerated carriers in the device. The addition of a P3HT EB layer (device B) does not cause large changes in the short-circuit EQE [Fig. 3(b)] but the increase of the photovoltaic active layer thickness reduces the short-circuit EQE. Compared to the control device, the short-circuit EQE is slightly reduced when PFB is used for the EB interlayer [device C, Fig. 3(c)] but it increases to 20% at -0.5 V and to 40% at -4 V.

The chemical structures of the polymers and the cross linker (FPA) used for this study. (b) Dark J-V curves for photodiodes made of device A (F8TBT:P3HT blend, open squares), device B (P3HT/ F8TBT:P3HT bilayer open circles), device C (PF8TBT/P3HT bilayer, open up triangles), and device D (TFB/F8TBT:P3HT/F8TBT multilayer, open down triangles). (c) Dark J-V curves of multilayer photodiodes made of device E (PF8TBT:P3HT/F8TBT) with a total film thickness of 120 nm (open squares), 140 nm (open circles), and 210 nm (open down triangles). The dark J-V curve of device E in which the F8TBT:P3HT was not photocross-linked is also depicted (nominal total film thickness 140 nm, solid circles). For all devices glass/ITO/PEDOT:PSS and Al were the hole-collecting (bottom) and electron-collecting (top) electrodes, respectively.
coating, using photocross-linking of underlying layers. Devices that use a photocross-linked electron-blocking layer adjacent to the PEDOT:PSS anode show good performance, but devices that require photocross-linking of the charge generating bulk polymer heterojunction are less effective due to caused changes associated with the cross-linking chemistry.

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For devices with both EB and HB layers (devices D and E), the short-circuit EQE is considerably reduced in respect to the control [Fig. 3(d)]. Based on experiments of thickness determination and of UV-Vis and PL spectroscopy of the F8TBT:P3HT 1:1 blend, before and after cross linking, we attribute the reduced EQE of the multilayer devices partially to the cross linking-induced disruption of the π-conjugation of the polymer backbones. When TFB is the EB layer (device D), the peak EQE recovers to ~5% at ~4 V [Fig. 3(d)] while maintaining a relatively low dark current density of 130 pA/mm² at that voltage [Fig. 2(b)]. When PFB is the EB layer (device E) the maximum EQE does not exceed 1%. In addition, the dark current density of device D is a little lower than device E presumably due to the additional annealing step followed in the device fabrication protocol. Thin TFB layers on PEDOT:PSS allow easy injection of holes into light-emissive polymers, and the results here indicate that hole transport in the reverse direction is also effective. In comparison to TFB, the lower ionization potential of PFB does not easily account for the lower EQE measured for device E. We note however that PFB has a considerably lower hole mobility than TFB and this may cause a reduced electric field to be present in the charge-generating bulk heterojunction layer.

In conclusion, we have described a method for device architecture that enables the controlled design and fabrication of multilayer polymeric photodiodes via successive spin coating, using photocross-linking of underlying layers. Devices that use a photocross-linked electron-blocking layer adjacent to the PEDOT:PSS anode show good performance, but devices that require photocross-linking of the charge generating bulk polymer heterojunction are less effective due to caused changes associated with the cross-linking chemistry.

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