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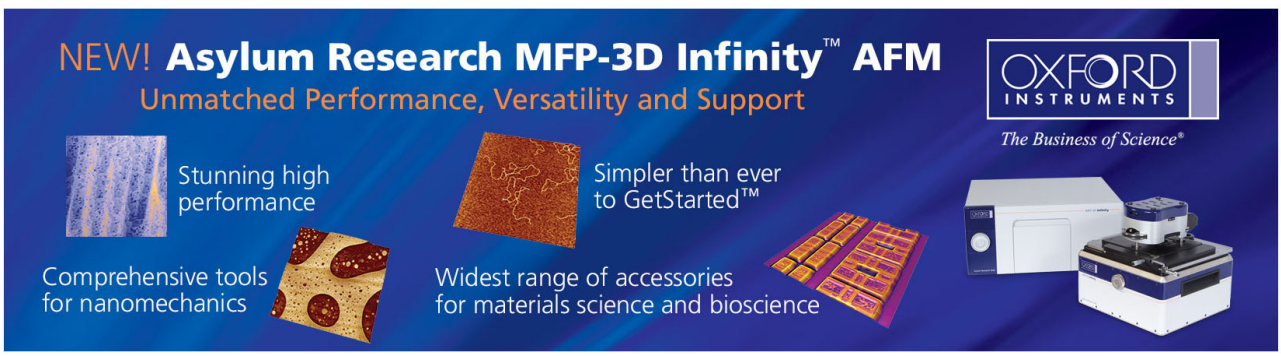

Increasing organic vertical carrier mobility for the application of high speed bilayered organic photodetector

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The direct influence of the vertical carrier mobility on the frequency response of bilayered organic photodiodes (PDs) is investigated for the first time. With fullerene as the acceptor material, changing vertical hole mobility from 2.3×10^{-5} to 2.8×10^{-4} $cm^2/V\,s$ increases PD bandwidth from 10 to 80 MHz under a 4 V operation. The influence of deposition rate on vertical hole mobility of pentacene film is also discussed. Our results facilitate the application of bilayered organic PDs on the detection of very-high-frequency optical signals. © *2009 American Institute of Physics*. [doi:10.1063/1.3263144]

Organic electronics has drawn lots of interest due to their low fabrication temperature on a variety of low-cost flexible substrates, thereby enabling the development of organic photonic integrated circuit, organic sensor array, organic photocouplers, or organic imaging sheets. For these applications, high speed organic photodetectors (PDs) are usually required. In organic PDs, photodetection is via the dissociation of photogenerated excitons at the interface between a donorlike material and an acceptorlike material. The performance of a PD is determined by the efficiency of charge generation and charge transport. The quantum efficiency of a PD can be enhanced by creating a bulk heterojunction, while the charge transport property can be improved by utilizing high mobility materials. However, the influence of carrier mobility on the PD response speed was never been clearly discussed. The frequency response of organic PDs is also rarely studied. Only a few reports demonstrated the frequency response of organic PDs.[1–3] The highest operation frequency (~430 MHz) of organic multilayer PDs was reported by using ultrahigh-vacuum (1×10^{-10} Torr) organic molecular-beam deposition to control the thickness of an individual layer as 0.5 nm to enable carrier tunneling.[1] When a conventional high vacuum (5×10^{-7} to 1×10^{-6} Torr) deposition system is used, a multilayered PD was reported to exhibit a bandwidth from a few kilohertz to a few megahertz under a operation voltage as 1–5 V and have a small incident photon to current conversion efficiency (IPCE) as 0.02%.[2] Another report used a bilayered structure to demonstrate a bandwidth as 70 MHz under a 7 V operation while the peak IPCE is around 7%.[3] In these studies, even high frequency responses are demonstrated, factors associated with organic materials to influence frequency response are not discussed. For a bilayered organic PD, response speed may be influenced by the separation of exciton, the carrier mobility, the multiple trapping and releasing procedure, the interface trapping, the RC delay due to the PD structure, etc. In this study, experiments are designed to show that the vertical carrier mobility is the dominant factor to influences the response speed of bilayered organic PDs. The influence of microstructure of organic film on the vertical carrier mobility is also explored. By utilizing commonly used organic molecules such as fullerene (C60) and pentacene, we proposed that the key to increase the speed of organic PD is to use materials with high vertical carrier mobility. A clear dependence between vertical carrier mobility and the frequency response of organic diodes and of organic PDs is verified. With C60 as the acceptor material, using high mobility pentacene in stead of poly(3-hexylthiophene) (P3HT) to serve as the hole transport layer effectively improves the hole mobility over one order and hence enlarges the operation bandwidth to be 80 MHz under a 4 V operation. The influence of deposition rate on the vertical mobility of pentacene film grown on poly (3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS) is also discussed for the first time.

Schematic cross sectional view of the bilayered PD is shown in the inset of Fig. 1(a). For the PDs with structure as indium tin oxide (ITO)/PEDOT:PSS/pentacene/C60/LiF/Al, the device made from pentacene deposited at high deposition rate (1 Å/s) is referred to Sample A (1 Å/s) while the device made from pentacene deposited at low deposition rate (0.1 Å/s) is referred to Sample A′ (0.1 Å/s). Sample B represents the PD with structure ITO/PEDOT:PSS/P3HT/C60/LiF/Al. The PD structures were fabricated on precleaned ITO glass substrate with a layer of 200 Å PEDOT:PSS. To investigate the influence of hole mobility on the response speed, pentacene and P3HT with identical thickness were used as donor materials and C60 was used as acceptor layer, respectively. P3HT was spin coated on PEDOT:PSS from toluene (1.5 wt %) and annealed at 200 °C for 10 min. Pentacene (0.1 or 1 Å/s) and C_{60} (1 Å/s) were deposited by thermal evaporation through shadow mask at a pressure as 1×10^{-6} torr at room temperature. The thickness of the donor and acceptor were 1000 and 500 Å, respectively. Then, the samples were transferred to deposit the cathode of LiF(10 Å)/Al(1000 Å). All the fabrication processes were in glove

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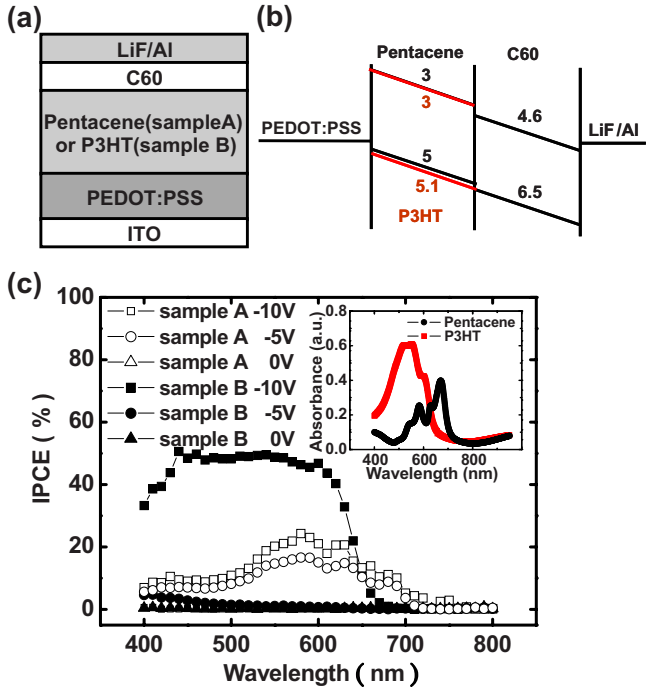

FIG. 1. (Color online) (a) Schematic device structure of the bilayered PD. (b) The energy band diagrams of sample A and sample B. (c) The incident photon-to-electron conversion efficiency of sample A and sample B under various reverse voltage biases. The inset shows the absorption spectra of pentacene and P3HT.

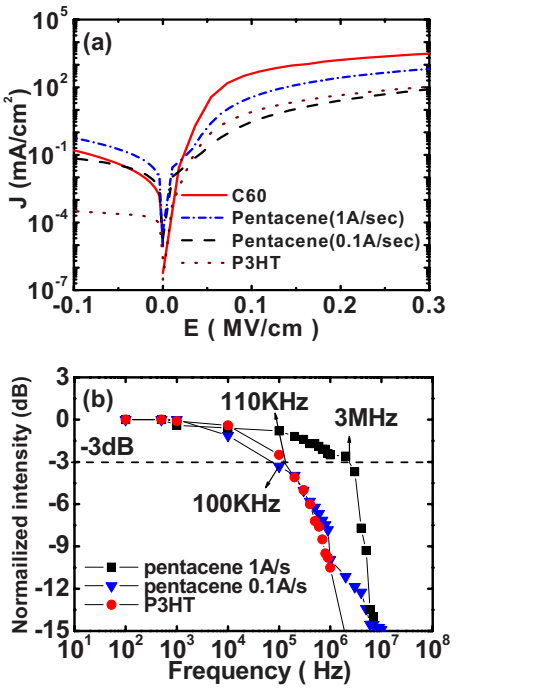

FIG. 2. (Color online) (a) The current density–voltage characteristics of organic diodes with C60, P3HT, pentacene deposited at 0.1 Å/s, and pentacene deposited at 1 Å/s. (b) The electrical frequency responses of pentacene diodes and P3HT diode. Characteristics of diodes made by pentacene films deposited at different deposition rate are compared.

box to immune the influence of water vapor and oxygen. The active region of the PDs was 4 mm^2. The devices are encapsulated by glass cap with UV glue in a glovebox, and measured in ambient condition. For transient response measurement, the laser diode with a wavelength as 633 nm (U-LD-650541A/B, Union Optronics Corp.) is used to trigger samples. The photocurrent from the PD was measured by using a Femto DHPCA-100 trans-impedance amplifier and the output signal is displayed on a digital oscilloscope (Gwinstek). Atomic force microscope (AFM) images were measured in tapping mode by Dimension 3100, Digital Instrument.

The energy band diagrams of sample A and sample B are shown in Fig. 1(b), while the incident photon-to-electron conversion efficiency (IPCE) of sample A and sample B under reverse voltage biases are compared in Fig. 1(c). The IPCE of sample A achieves 24% at 580 nm at a reverse bias of 10 V and remains 10.1% at 690 nm. As for sample B, the IPCE is around 45%–50% at a reverse bias of 10 V in the range from 420 to 620 nm. A sharply decrease in IPCE start at 620 nm and the IPCE lower than 10% is observed over 650 nm. Sample A absorbs more effectively than sample B in the range from 650 to 690 nm. This results from the difference in absorption spectra of pentacene and P3HT as shown in the inset of Fig. 1(c). Changing pentacene deposition rate has no significant influence on IPCE curves or on absorption spectrum.

As a first step to understand the influence of the mobility on the frequency response of PD, the vertical carrier mobility of C60 and pentacene are extracted from the space-charged-limited current of organic diodes.[4] Figure 2(a) compares the current density–voltage characteristics of organic diodes with C60, P3HT, pentacene deposited at 0.1 Å/s, and pentacene deposited at 1 Å/s. The thickness of organic layer is fixed as 180 nm. The vertical carrier mobility is 1.9×10^{-3}, 6.0×10^{-5}, 2.3×10^{-5}, and 2.8×10^{-4} $cm^2/V\,s$ for C60, P3HT, pentacene (0.1 Å/s), and pentacene (1 Å/s), respectively. The carrier mobility in C60 is much higher than that in P3HT or in pentacene, implying that the response bottleneck in organic PDs is usually in donor material rather than in acceptor material. Hence, it is essential to obtain high vertical hole mobility in donor material. To demonstrate the influence of vertical hole mobility on the electrical frequency response of the diode, the frequency responses of P3HT diodes and pentacene diodes measured in a rectifier circuit are compared in Fig. 2(b). A function generator (8110A Pulse Pattern Generator, Agilent) is used to supply the ac input signals. A capacitor as 0.1 μF and the internal resistance of the oscilloscope as 10 MΩ are used as the load capacitor and the load resistance in the rectifier circuit.[5] The high hole mobility in pentacene (1 Å/s) contributes to a large bandwidth as 3 MHz while the low hole mobilities in P3HT and pentacene (0.1 Å/s) make the P3HT and pentacene (1 Å/s) diodes lose their rectifying ability at a frequency about 100 kHz.

Then, the frequency responses of PDs (samples A, A′, and B) are compared in Fig. 3 by plotting the normalized output amplitude versus the frequency of the input signal varies from 100 Hz to 50 MHz. The schematic measurement setup is shown in the inset. The input signal is the light generated by a laser diode with a wavelength as 633 nm. The laser diode is switched on and off by a square-wave voltage signal with different frequencies. Samples are reverse biased at 4 V during measurement. It is found that the frequency response of sample B is similar to that of sample A′ (0.1 Å/s) while Sample A (1 Å/s) follows the input signal well even under a 50 MHz light switching. Though the pulse generator in our experiment has a frequency limitation of 60 MHz, the bandwidth of Sample A can be estimated by fitting

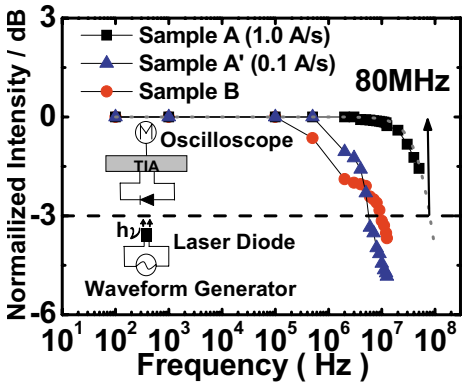

FIG. 3. (Color online) The frequency characteristics of PDs made by pentacene and P3HT. Characteristics of PDs made by pentacene films deposited at different deposition rate are compared. The gray dotted line is calculated following $P=P_0/(1+f/f_C)$. The schematic measurement setup is shown in the inset.

the experimental data with the basic transfer function of a single-time-constant low-pass amplifier.[3,6] The dashed line in Fig. 3 represents the calculated normalized output power intensity as a function of frequency. A 80 MHz bandwidth can be expected for sample A under a 4 V operation.

As aforementioned, the response bottleneck is in the donor material. Our results reveal a significant influence of pentacene deposition rate on the vertical hole mobility and on the PD bandwidth. For pentacene grown on PEDOT:PSS, it is reported that a deposition rate higher than 3 Å/s leads to high nucleation sites and small grain size.[7] In our experiment, the AFM images of 100-nm-thick pentacene films deposited at 0.1 or 1 Å/s on PEDOT:PSS are shown in Figs. 4(a) and 4(b), respectively. Grain size and grain structure of these two images are similar to each other. Thin-film x-ray diffraction patterns of these two samples (not shown) are also almost identical. It is therefore speculated that the deposition rate (0.1 or 1 Å/s) has no significant influence on pentacene bulk region. The difference in the initial growth stage may play an important role to influence the observed vertical hole mobility. To verify the speculation, we compares the AFM images of 1.5-nm-thick pentacene films deposited at 0.1 or 1 Å/s on PEDOT:PSS as shown in Figs. 4(c) and 4(d), respectively. The AFM images of 3-nm-thick pentacene films deposited at 0.1 or 1 Å/s on PEDOT:PSS are also shown in Figs. 4(e) and 4(f). As shown in Fig. 4(f), the 3-nm-thick pentacene deposited at 1 Å/s on PEDOT:PSS starts to develop dendritic structures. The 3-nm-thick pentacene film deposited at 0.1 Å/s on PEDOT:PSS as shown in Fig. 4(e), however, has no clear grain structure yet. Since the PEDOT:PSS exhibits a hydrophilic surface, it is proposed that pentacene grown on PEDOT:PSS follows "layer-plus-island" (Stranski–Krastanov) mode.[8] When pentacene molecules arrive on PEDOT:PSS, they rearrange and pack to form two-dimensional islands due to the strong interaction between pentacene molecules and substrate. After the formation of the first few monolayers to cover the substrate, pentacene growth mode turns to the island mode that forms three-dimensional islands when the interaction between pentacene molecules is stronger than the interaction between pentacene and substrate. Decreasing the deposition rate may reduce the surface coverage.[9] Because low deposition rate creates low nucleus density, molecules have to diffuse a larger distance to be incorporated into islands, hence have a larger possibility of being desorbed. As a result, in our study, lower deposition rate retards the formation of three-dimensional islands. On the other hand, pentacene deposited at 1 Å/s on PEDOT:PSS exhibits more three-dimensional islands, leading to the improvement of film order in the vertical direction and the increase of vertical mobility.

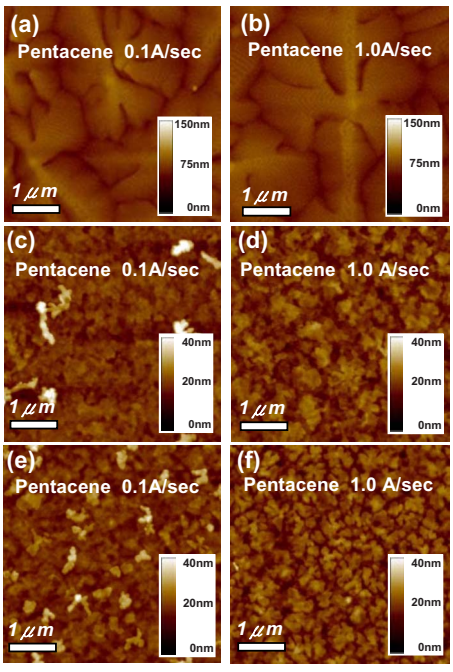

FIG. 4. (Color online) AFM images of 100, 1.5, and 3 nm pentacene films deposited at (a) 0.1 Å/s and (b) 1 Å/s, (c) 0.1 Å/s and (d) 1 Å/s, and (e) 0.1 Å/s and (f) 1 Å/s on PEDOT:PSS covered ITO glass, respectively.

In summery, we report a direct influence of the vertical carrier mobility on the response speed of organic PDs. By using C60 as the acceptor material and pentacene with high deposition rate as the donor material, a high-speed bilayered organic PD is demonstrated for the detection of very-high-frequency (VHF, >30 MHz) light switching signals. The influence of deposition rate on the vertical hole mobility of pentacene on PEDOT:PSS is investigated and explained. The VHF organic PDs facilitate the development of the next-generation information technologies.

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