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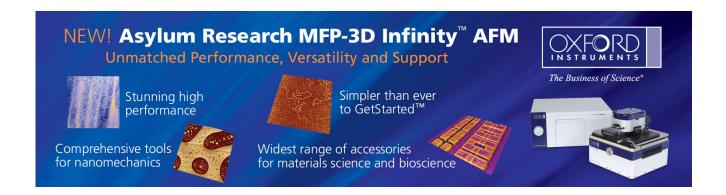
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# Polymer hot-carrier transistor with low bandgap emitter

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Vertical polymer hot-carrier transistor using the low bandgap material poly(3-hexylthiophene) as both the emitter and the collector are studied. The common emitter current gain is shown to depend on the LiF thickness and the emitter thickness, with maximal value at 31. Current density as high as 31 mA/cm² is achieved when collector voltage is −10 V. For the device using blend of poly(3-hexylthiophene) and high bandgap polymer poly(9-vinylcarbazole) as the emitter, the current density rises sharply to 428 mA/cm². The brightness of 3000 cd/m² is obtained as a polymer light-emitting diode is driven by the transistor with the same area. The transistor can be operated at 100 kHz. © 2008 American Institute of Physics. [DOI: 10.1063/1.2839395]

Conjugated polymers have received great attention because of its applications in light-emitting diode, solar cell, and transistor by solution process. There are two types of polymer transistors, namely, the conventional field-effect transistor (FET) and the vertical metal-based transistor. 1-6 Due to its potential to overcome the limit of FET, recently metal-base organic transistors, including the space-chargelimited transistor<sup>4</sup> and hot-carrier transistor,<sup>5</sup> gain more and more attention for both polymer and small molecules.<sup>2</sup> Previously, a high bandgap organic semiconductor poly(9vinylcarbazole) (PVK) is selected for the emitter in order to maximize the energy barrier at the emitter-base junction, thus enhancing the hot-carrier kinetic energy and reducing the base current.<sup>5</sup> Even though reasonable common emitter current gain  $\beta$  is achieved, the high bandgap emitter comes at a great cost. The high bandgap implies a large barrier for the holes to be injected from the metal contact to the emitter valance band.<sup>8</sup> Depending on the surface contamination level, the work function of emitter electrode Au can vary from 4.7 to 5.1 eV. The ionization potential of PVK is 5.8 eV, implying a large hole injection barrier of 0.7–1.1 eV. The resulting collector density is therefore as low as 0.56 mA/cm<sup>2</sup>. Similar low current density also occurs in hot-carrier transistor based on evaporated small molecules.

In this work, we replace the high bandgap emitter by a low bandgap polymer poly(3-hexylthiophene) (P3HT) with ionization potential (IP) at 5.1 eV, which is much closer to the Au work function than PVK. In fact, P3HT is also the material used for the collector. There is, therefore, no energy offset between emitter and collector valence band which is usually required for the hot-carrier collection. Similar to the case of PVK emitter, a thin layer of LiF is used as the tunneling barrier to enhance the relative energy. Unlike the PVK device where LiF is only auxiliary to create the hot-carrier energy offset above the collector band edge, for P3HT emitter, the energy offset depends entirely on the LiF layer. The

The device structure of the hot-carrier transistor in this work is indium tin oxide (ITO)/PEDOT:PSS/P3HT(C)/Al(B)/Al<sub>2</sub>O<sub>3</sub>/LiF/P3HT(E)/Au. P3HT is used as both the emitter (E) and collector (C). The middle Al layer is the base (B), and the top Au layer is the emitter contact. Figure 1 shows the energy band profile of hot-carrier transistor in the active mode. The thin LiF/Al<sub>2</sub>O<sub>3</sub> layer is the tunneling barrier which further separates the emitter valence band and the base Fermi level by a voltage drop across it. The device is fabricated on cleaned ITO substrate, and a 300 Å PEDOT-

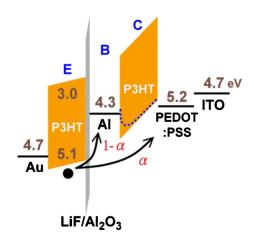


FIG. 1. (Color online) The energy band profile of the polymer hot-carrier transistor in the active mode. The energies are indicated in eV.

prerequisite of hot-carrier transistor using low bandgap emitter is, therefore, that the tunneling barrier alone must be able to maintain a good common emitter current gain. It turns out that the common emitter current gain is not compromised even without the high bandgap emitter, indicating that the tunneling barrier is more crucial than the semiconductor band positions for the operation of the transistor. As for the collector current density, it increases dramatically from 0.56 mA/cm² for PVK emitter to several tens of mA/cm² for P3HT emitter. We demonstrate that this transistor is able to drive a polymer light-emitting diode with the same area up to brightness of thousands of cd/m².

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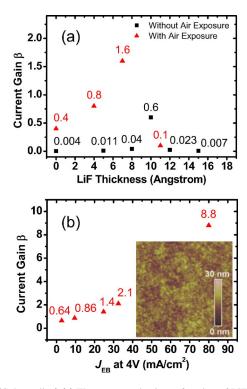


FIG. 2. (Color online) (a) The current gain  $\beta$  as a function of LiF thickness of the hot-carrier transistor. The solid square (solid triangular) indicates the device without (with) exposure to air after Al deposition. The current gain is obtained in the common emitter configuration with  $V_E$  is 0 V,  $V_C$  is -5 V, and  $J_B$  is 2 mA/cm². (b) The current gain  $\beta$  as a function of EB diode current density at 4 V. The current gain is obtained in the common emitter configuration with  $V_E$  is 0 V,  $V_C$  is -5 V, and  $J_B$  is 2.5 mA/cm². The inset shows the AFM image of Al base on P3HT with roughness of 2.6 nm. The height scale is 30 nm and the dimensions of the image is  $5 \times 5 \ \mu m^2$ .

:PSS layer is spin coated. P3HT is then spin coated to form the 1200 Å collector layer. A thin Al film around 80 Å is evaporated (10 Å/s) as the base through a shadow mask, followed by a LiF layer of various thicknesses. The optimal  $Al_2O_3$  layer is formed by air exposure for 3 min after Al deposition. The oxidation time for the Al is limited to be 3 min since a 15 Å Al can be completely oxidized in 5 min. Another P3HT layer is spin coated from xylene (2 wt %) to form 320 Å emitter layer. Au is evaporated as the emitter contact. The active area is 2 mm². The devices are encapsulated by glass cap with UV glue in a glovebox, and measured in ambient condition. The sign convention throughout the text is that when holes leave from the base and collector,  $J_B$  and  $J_C$  are positive.

Figure 2(a) shows the  $\beta$  of hot-carrier transistor with different LiF layer thicknesses with or without  $Al_2O_3$  layer in the common emitter configuration. For transistor without  $Al_2O_3$ ,  $\beta$  initially increases with increasing LiF thickness, and reaches a maximum  $\beta$ =0.6 when LiF thickness is 10 Å. For LiF thickness higher than 10 Å,  $\beta$  decreases due to the insulating nature of LiF. For the transistor with  $Al_2O_3$ ,  $\beta$  also has a maximum value of 1.6 when LiF thickness is 7 Å. The inset in Fig. 2(b) shows the atomic force microscopy (AFM) image of Al base on P3HT. No pinhole can be observed. In addition, the roughness of 2.6 nm is much smaller than the mean thickness of the Al base.

As LiF thickness increases, the tunneling barrier forms gradually, and the voltage drop across the LiF layer develops. Hence, the energy barrier at emitter-base junction is enlarged and the hot-carrier loss to base reduced. However,

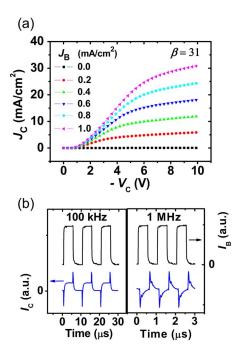


FIG. 3. (Color online) (a) The characteristics of the polymer hot-carrier transistor in common emitter configuration. The emitter layer is P3HT. (b) Frequency response of the hot-carrier transistor under modulation at 100 kHz and 1 MHz.

as the thickness is too large, the LiF layer becomes an insulator which blocks all carriers and the collector current density  $J_C$  becomes very small. The residual base current due to the reverse current of the base-collector diode then dominates and causes a small  $\beta$ . In general,  $\beta$  is much higher for devices with Al<sub>2</sub>O<sub>3</sub> layer, and the maximal  $\beta$  occurs at smaller LiF thickness. The transistor with Al<sub>2</sub>O<sub>3</sub> needs less LiF to achieve maximal  $\beta$  since there is a ultrathin Al<sub>2</sub>O<sub>3</sub> before LiF deposition. The Al<sub>2</sub>O<sub>3</sub> grown in air is dense with a much better insulating property than LiF, so it may serve as a better tunneling barrier than LiF. Furthermore, the Al<sub>2</sub>O<sub>3</sub> may prevent the reaction between Al and LiF which will release Li atom and reduce the thickness of the LiF.

In addition to insulator thickness,  $\beta$  is also sensitive to the emitter thickness. A series of hot-carrier transistor with Al<sub>2</sub>O<sub>3</sub> and 7 Å LiF, with various emitter thicknesses from 600 to 250 Å is fabricated. The emitter-base diode is fixed at a forward bias  $V_{EB} = V_E - V_B$  of 4 V. The emitter-base diode current density  $J_{EB}$  increases from 2.7 to 80 mA/cm<sup>2</sup> as the emitter thickness decreases from 600 to 250 Å. Figure 2(b) shows the relationship between  $\beta$  and  $J_{EB}$ . The  $\beta$  increases with increasing  $J_{EB}$  and decreasing emitter thickness. The highest  $\beta$ =8.8 is obtained when  $J_{EB}$  is around 80 mA/cm<sup>2</sup> at 4 V. Initially,  $V_{EB}$  increases with increasing  $|V_C|$  then saturates.  $V_{EB}$  at  $V_C$ =-10 V and  $J_B$ =2.5 mA/cm<sup>2</sup> decreases from 3.9 to 2.5 V with decreasing emitter thickness. For thin thickness, a small  $V_{EB}$  is needed to obtain a specific  $J_B$ , so base-collector voltage  $V_{BC} = V_B - V_C$  is larger for given  $V_C$ . The image-force lowering effect at the base collector becomes strong, as shown by the dotted line in Fig. 1. The effective barrier between the base and collector is therefore reduced further and hot-carrier collection more efficient.

Under optimal conditions, the characteristics of the hotcarrier transistor using P3HT as both the emitter and collector is shown in Fig. 3(a). With the lower injection barrier from the Au anode, the collector current density  $J_C$  reaches as high as 31 mA/cm<sup>2</sup>, a dramatic increase from the previous work using high bandgap emitter PVK by two orders of magnitude.  $\beta$  is 31. This value is similar to the case of PVK suggesting that the hot-carrier collection is not compromised by the lower hot-carrier energy as long as LiF layer is used. Even though there is no energy offset between the emitter and the collector semiconductor, Fig. 3(a) shows that the tunneling barrier alone is enough to produce a reasonable  $\beta$ with proper thickness. The transistor shows quite pronounced saturation as the collector voltage increases. In addition to high  $\beta$  and density, hot-carrier transistor has an intrinsic fast response because the effective channel length is defined by the film thickness which is only 150 nm. Figure 3(b) shows the response of the transistor under modulation at 100 kHz and 1 MHz square wave applied between the base and emitter. The collector current is registered by the voltage across a  $100~\Omega$  resistor in series. The collector current follows the square wave up to 100 kHz. At 1 MHz, the output waveform is distorted but still responding. Polymer hot-carrier transistor is, therefore, promising for high speed applications in the radio frequency.

Finally, we study the hot-carrier transistor whose emitter is a blend of low and high bandgap materials. P3HT and PVK are blended in toluene solution (1:5 wt/wt) with the total polymer concentration of 6 wt % and spin coated at 8000 rpm to form the emitter. The current density of emitterbase diode at  $V_{EB}$ =4 V is 126 mA/cm<sup>2</sup>. This transistor is measured in the common emitter configuration when  $V_E$ =0 V,  $V_C$ =-10 V, and  $J_B$ =5 mA/cm<sup>2</sup>. The collector current density  $J_C$  is 126 mA/cm<sup>2</sup>,  $\beta$  is 25, and on/off ratio is 468. When  $J_B$  increases to 40 mA/cm<sup>2</sup>, the output current density is as high as 428 mA/cm<sup>2</sup>,  $\beta$  is 11, and on/off ratio is 1751. Unlike pure P3HT transistor in Fig. 3(a), the blend transistor in Fig. 4(a) somehow does not show a tendency for saturation. AFM image shows a rough surface with rootmean-square value of 20 nm. The roughness may increase the contact area between Au and emitter. In addition, some carriers could be injected stepwise from Au to P3HT, and then finally to PVK. The hot carriers in metal base from PVK have higher energy than those from P3HT, and are easier to cross the base-collector junction barrier and contribute to the collector current.

Now, the current density of the hot-carrier transistor is high enough to drive a PLED, the ITO collector of the hot-carrier transistor and the ITO anode of the PLED are connected to demonstrate their integration. The PLED has the structure ITO/PEDOT/PPV(SuperYellow)/CsF/Al. The Au electrode of hot-carrier transistor is grounded, and the cathode voltage of the PLED is kept constant at -10 V. Figure 4(b) shows the luminance of the PLED at various  $J_B$ . The luminance of the PLED driven by the hot-carrier transistor can be over  $3000 \text{ cd/m}^2$ , which is enough for most applications.

In conclusion, we show that the high bandgap semiconductor is not necessary for the emitter in organic hot-carrier

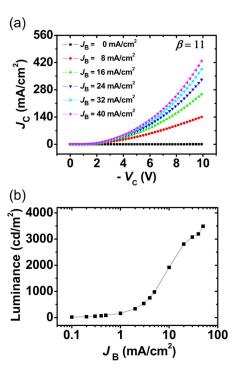


FIG. 4. (Color online) (a) The characteristics of the polymer hot-carrier transistor in common emitter configuration. The emitter layer composed of P3HT and PVK in weight ratio 1:5. (b) The luminance of the polymer light-emitting diode driven by the polymer hot-carrier transistor operated in various base current densities.

transistor in order to achieve a high common emitter current gain. Now, the hot-carrier transistor is good enough to drive a polymer light-emitting diode to high brightness, and it can be operated at a high frequency.

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