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Yu-Chiang Chao, Syuan-Ling Yang, Hsin-Fei Meng, and Sheng-Fu Horng

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Polymer hot-carrier transistor

Yu-Chiang Chao, Syuan-Ling Yang, and Hsin-Fei Meng^{a)}

Institute of Physics, National Chiao Tung University, Hsinchu 300, Taiwan, Republic of China

Sheng-Fu Horng

Department of Electric Engineering, National Tsing Hua University, Hsinchu 300, Taiwan, Republic of China

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Metal-base hot-carrier transistor with conjugated polymer emitter and collector is demonstrated. The device is fabricated by multiple spin coating with the metal base sandwiched between two polymers. A thin insulating layer of LiF is inserted between the emitter and base to enhance the hot carrier kinetic energy and reduce mutual dissolution. Using poly(9-vinylcarbazole) as the emitter, Al as the base, and poly(3-hexylthiophene) as the collector, common-emitter current gain of 25 is obtained with operation voltage as low as 5 V. © 2005 American Institute of Physics.

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Polymer-based organic transistors provide a promising future for large-area and low-cost applications in display technology, sensors, and radio frequency identification cards from the perspectives of their easy solution process as well as the potential integration with organic optoelectronics.¹⁻⁴ Polymer field-effect transistors (FETs) are mostly horizontal devices in which source and drain electrodes lie in the same plane of the substrate. The highest polymer hole mobility of about $0.1 \text{ cm}^2/\text{V s}$ is reported for poly(3-hexylthiophene) (P3HT) FET^{1,5} a few years ago. Beyond this value little progress has been made. Due to the limited mobility, such horizontal devices are not candidates for high current and high frequency application unless the channel length is made submicron. Consequently, how to shrink the channel length in polymer FET has been a demanding issue. Though the well developed technology of submicron lithography can be directly applied to reduce the polymer FET channel length, this strategy is in opposition to the advantages of low-cost and large-area solution process unique to conjugated polymers.

Polymer FET with vertical channel has been proposed to achieve submicron channel length. For vertical polymer FET the channel length is defined by the thickness of the layer. However, in order to realize a vertical FET channel one usually needs to employ an unreliable mechanical method like embossing.⁶ Aside from FET, the bipolar junction transistor (BJT) is a successful vertical device with high current and high frequency for inorganic semiconductors. BJT consists of two back-to-back *pn* junctions formed by heavily doped base (*B*), emitter (*E*) and collector (*C*). In principle this device structure can be applied to conjugated polymer using multiply spin coating. The thickness and therefore the effective channel length can be reduced down to 10 nm. However, the major problem is that the base layer needs to have low resistance in order to maintain a uniform voltage throughout the active area and reduce the emitter-to-collector transient time. Even for heavily doped conducting polymer, the resistivity is too large to serve as the base material. Despite of its

vertical nature, polymer BJT is therefore quite unlikely to succeed.

In this letter we present a vertical polymer hot-carrier transistor with metal base, which combines the advantage of short effective channel length, low base resistivity, and easy large-area solution process. Glass substrate is used for easy integration with organic light-emitting diodes. Similar to BJT, in hot-carrier transistor the carriers are injected from the emitter into the base. Because of the large energy barrier at the emitter-base junction, they become hot carriers in the metal. Assuming the metal is thinner than the mean free path of the carrier, most of the injected carriers will be collected by the collector. The ratio is called the transport factor α , which plays the same role as the transport factor in BJT. Large current amplification results from α close to one. Current gain β is defined as $\alpha/1-\alpha$. In fact, for silicon BJT, the replacement of semiconductor base by metal was proposed in the early 1960s.⁷ However, since silicon is a nearly perfect crystal, the backscattering of carrier at the base-collector junction is severe as the interface varies abruptly. The current gain β is therefore usually poor. A similar idea of using C₆₀ as the emitter but still utilizing silicon as the collector is recently reported.^{8,9} But such device turns out to be a permeable base transistor instead of the hot-carrier one. Because of the disorder of polymer and that the interface does not vary so abruptly, we expect the backscattering in our case will not be as severe as in silicon hot-carrier transistor and higher β is expected. Indeed we found that high current gain with low operation voltage can be realized in polymer hot-carrier transistor. Interestingly, in addition to the base for hot-carrier transistor, metal sandwiched between organic semiconductors has been shown to exhibit current memory effect,¹⁰ and transistor-like device can be made based on such an effect.¹¹

The multilayer structure of the polymer metal-base transistor is indium tin oxide (ITO) glass/P3HT/Al/LiF/PVK/Au. P3HT is used as the collector because of the small Schottky barrier with Al and high mobility. PVK is poly(9-vinylcarbazole), which is used as emitter because of the large Schottky barrier with Al. Figure 1 shows the energy band profile of hot-carrier transistor in the active mode, i.e., the base-emitter (*BE*) junction is forward biased while the base-collector (*BC*) junction reverse biased. The hot carrier in our

^{a)} Author to whom correspondence should be addressed; electronic mail: meng@mail.nctu.edu.tw

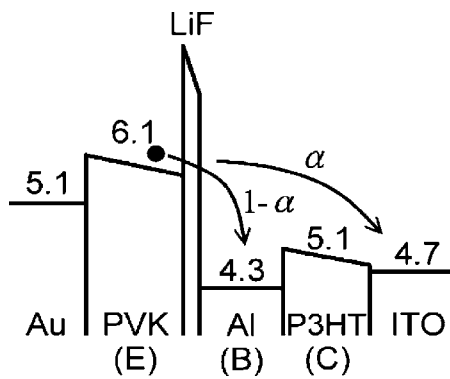


FIG. 1. The energy band profile of metal-base hot-carrier transistor in the active mode. The negatives of the actual energy are shown in order to illustrate the picture of holes better. The energies are indicated in eV.

device is hole. In order to illustrate the picture of hole, the negative of all the energy levels is shown. The work function of Au and Al are 5.1 and 4.3 eV, respectively. The lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) for PVK are 2.3 and 6.1 eV below the vacuum level, and those for P3HT are 3 and 5.1 eV, respectively. Note that LUMOs of the polymers are irrelevant to the device operation and not shown. The resultant energy barrier between base and emitter is as large as 1.8 eV, which enables the holes to be far above the Fermi level (i.e., hot carrier) when passing through the thin metal base. The hot holes are expected to have such a high kinetic energy that they are easily injected into the collector since the collector-base barrier is less than that of emitter-base by 1 eV. In addition to the energy level requirements, the base layer thickness must be less than the mean free path for the hot hole in the base in order to reduce the probability of hole capture by the base through inelastic scattering.¹² The mean free path of Al is about 100 Å.¹³ The unwanted electron current is negligible because the electron injection barrier from Al to PVK is 2 eV, and 1.7 eV from ITO to P3HT. Under active mode bias, holes are injected into the HOMO of PVK from the Au electrode, followed by tunneling through the LiF layer and passing ballistically across the base high above the Fermi level. Because P3HT is not crystalline, the quantum mechanical reflection at the base-collector interface which has plagued the inorganic hot-carrier transistor will not happen here. The LiF layer between emitter and base is intended to provide two advantages. First, the voltage drop across LiF lowers the Al Fermi level relative to HOMO of PVK and further increases the energy difference between PVK and P3HT. Hence the holes have higher kinetic energy in base with LiF. Second, the LiF layer serves as a protection layer which prevents the P3HT from possible dissolution when spin coating PVK. Indeed, the insertion of LiF layer enhances the device stability and reproducibility. The I - V curve of EB and BC junctions shown in Fig. 2 demonstrate good diode characteristic with rectification ratio of about 10^3 and 10^5 , respectively.

The device is fabricated on patterned ITO glass substrate cleaned by de-ionized water, acetone and 2-propanol consecutively in ultrasonic bath. Fourteen hundred angstroms of P3HT is spun cast from chloroform solution (1.2 wt%) onto the substrate, followed by a thin aluminum film of 90 Å evaporated as the base at 0.2 Å/s through a shadow mask. To wire out the base, a 1000 Å Al strip is deposited with

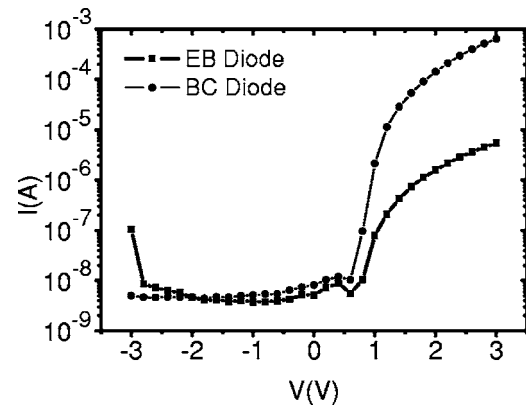


FIG. 2. The I - V curves of emitter-base and base-collector diodes.

another shadow mask. LiF layer of 28 Å is deposited on the thin Al film, followed by 3300 Å of PVK spun cast from toluene solution (7 wt%) to form the emitter. Gold is deposited as the emitter contact. The devices are packaged in a glovebox and all electrical measurements are performed in ambient condition. The polymers are purchased from Aldrich. All metal layers are deposited in a chamber having a base pressure of 1.0×10^{-6} mbar. The device active area, defined by crossover between the Au and ITO electrode, is 4 mm². The thickness of each polymer layer is measured by Kosaka ET4000 surface profiler. Current-voltage curves are measured by a HP 4157 semiconductor parameter analyzer.

Figure 3 shows the characteristics of hot-carrier metal base transistor in the common-emitter configuration. The emitter Au electrode is commonly grounded and the ITO electrode is negatively biased at V_C with respect to Au. The collector current I_C does increase with the base current I_B . The common-emitter current gain β is 25 when V_C is -5 V. β is the average of five current gains at different I_B . Each current gain is given by $[I_C - I_C(I_B=0)]/I_B$. However, for fixed I_B , $|I_C|$ increases with $|V_C|$ without saturation. This is probably due to the image-force barrier lowering at the BC junction and β increases with $|V_C|$.^{14,15} In Fig. 4, the voltage drop across the EB and BC junctions are plotted as functions of V_C at fixed $I_B = -0.2 \mu\text{A}$. The BC voltage drop $V_{BC} = V_B - V_C$ increases with $|V_C|$ while the EB voltage drop $V_{EB} = V_E - V_B$ is nearly a constant after $|V_C|$ exceeds 2 V. This behavior implies that further increase of $|V_C|$ mostly falls on

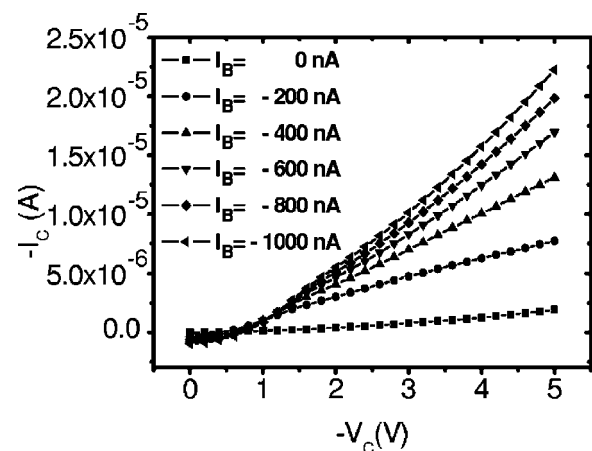


FIG. 3. The characteristics of the polymer hot-carrier metal-base transistor in common-emitter configuration.

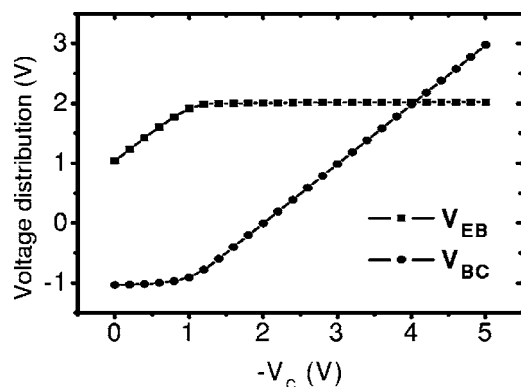


FIG. 4. The voltage drop across the emitter-base and base-collector junctions.

the reverse biased *BC* junction as expected. Common-base measurement shows consistent results. When V_C is -5 V and the base electrode is open, the I_C leakage current is $1.9 \mu\text{A}$ as shown in Fig. 3. Since the reverse current for *BC* junction is of the order nA as shown in Fig. 2, the leakage current is believed to result from some unexpected path caused by residual mutual dissolution of PVK and P3HT outside the active area. I_C leakage can be in principle reduced to a few nA if process control is improved. Au migration into PVK layer during the evaporation may reduce the effective resistance of PVK layer, and consequently the device has a small turn-on voltage despite the large hole injection barrier at Au/PVK junction. Finally, from the atomic force microscope image of the base metal, the Al roughness is less than two nanometers and no pinholes can be seen. It shows that our metal-base hot-carrier transistor is not in fact a permeable base one.^{9,16} The device reported in this letter is therefore the first organic hot-carrier transistor.

In summary, a solution-processed vertical polymer hot-carrier transistor is demonstrated to have current gain of 25. This device has high current output and low operation voltage. The active area can be made arbitrarily large and no lithography is needed. The use of LiF tunneling barrier not only improves the hot carrier kinetic energy and current gain but also serves as a protecting layer to prevent mutual dissolution between the polymers.

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