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Polymer space-charge-limited transistor

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A metal grid is sandwiched between poly(3-hexylthiophene) to form a solid-state version of vacuum tube triode, where the vertical space-charge-limited current is modulated by the grid potential. The Al grid contains random submicron openings formed by a nonlithographic method. The multilayer polymer structure is made by spin coating. The operating voltage of the polymer space-charge-limited transistor is 3 V, and the current gain of 506 is obtained. The characteristics of the transistor can be tuned by the diameters and the density of the openings on the grid. Similar to the vacuum tube triode, the current follows a power law voltage dependence. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2207838]

Electronic devices based on organic semiconductors provide attractive alternatives to inorganic devices due to their lower cost as well as the compatibility with flexible substrates. One of the key components in the organic electronic circuits is the polymer field-effect transistor (FET).[1,2] Many researches on polymer FET have demonstrated reasonable performance[3,4] and the possibility of integration with organic light-emitting diodes.[4–7] Current polymer field-effect transistors are mostly horizontal ones in which source and drain electrodes lie in the same plane of the substrate. Due to the intrinsically low carrier mobility in conjugated polymers relative to inorganic semiconductors and the expensive lithography process for reducing the channel lengths to the submicron, some research efforts were made on the vertical type FET in which the channel length is defined by the thickness of the insulating layer vertically separating the drain and source electrodes.[8–10] However, so far most techniques utilized in vertical-channel organic FETs do not take advantages of the low-cost and large-area solution process unique to conjugated polymers.

To circumvent the limits of both horizontal and vertical FETs, vertical non-field-effect organic transistors with multilayer structures were reported.[11–18] In these devices the channel length is defined by the total thickness of the organic layer and the current is modulated by a highly conductive layer embedded in the organic material. One example is the organic static-induced transistor (SIT) with a striped metal layer embedded in the thermally evaporated organic layer.[14,16] It has a similar structure with the vacuum tube triode, which consists of the cathode for electron emissions by heating, the anode for electron collection, and the grid for current modulation. In a vacuum tube triode both the grid and anode electrodes are able to control the potential within the device but the grid is much more effective in controlling the gradient near the cathode. When the grid is in large and negative bias, the electrons experience a negative gradient of potential after they are emitted from cathode. Effectively the electrons encounter a large energy barrier between cathode and anode, and consequently very few of them can be collected by the anode. On the contrary, if the grid is slightly negative biased or positively biased, it is possible for the electrons to find a passage through the potential minimum between two grid wires. Despite similar structure, in SIT the current is modulated by a junction potential barrier while in vacuum tube triode the space-charge-limited current (SCLC) is modulated.[19]

In 1952 Schockley proposed the "analog transistors" as the first solid-state device whose operation resembles that in the vacuum tube triode with current limited by the SCLC.[20] While SCLC is not the most common mode of transport in high-mobility inorganic semiconductors, in organic semiconductors it is well known that the current is governed by SCLC. Therefore, conjugated polymer might be one candidate for the vertical non-FET analog transistor.[17,18] In this letter we present a vertical polymer version of solid-state vacuum tube triode with an embedded metal grid. A more transparent name "space-charge-limited transistor" is given to this device. The metal grid made of Al film with random openings functions similarly to the grid in vacuum tube triode. The fabrication processes of polymer space-charge-limited transistor have both the advantages of short channel length and easy large-area solution processes. The carriers in the transistor are injected from the emitter, going through the openings on the metal grid and finally arriving at the collector. The potential distribution between emitter and collector can be controlled by the voltages of grid and collector. When the voltages of the grid and collector constitute a high barrier between the emitter and the opening, few carriers can arrive at the collector through the openings. On the other hand, if there is no barrier the carriers can go through the opening and reach the collector. The magnitude of the collector current is determined by the SCLC given by the potential difference between the emitter and the center of the opening. Collector current is modulated by the grid which controls the effective potential at the opening for fixed emitter and collector potentials.

The multilayer structure of the polymer space-charge-limited transistor is indium tin oxide (ITO) glass/PEDOT:PSS/P3HT/Al grid/P3HT/Al, as shown in Fig. 1(a). P3HT is poly(3-hexylthiophene) which is used as the semiconducting polymer between the electrodes. PEDOT:PSS is poly(3,4-ethylenedioxythiophene) doped with polystyrene

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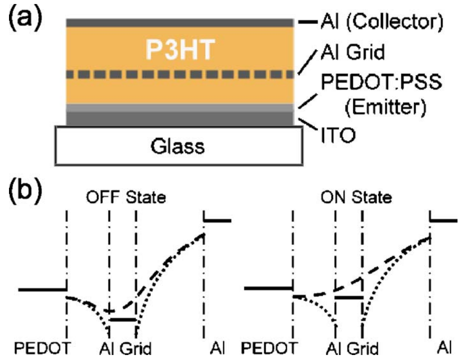

FIG. 1. (Color online) (a) Device structure of the polymer space-charge-limited transistor. (b) The potential profile for the on and off states of the transistor. The dash line is along the channel through the grid opening, while the dotted line is along the grid electrode. The solid line is the Fermi level of Al and PEDOT.

sulfonated acid. PEDOT:PSS with a work function of 5.2 eV serves as an Ohmic contact for hole injection into the highest occupied molecular orbital (HOMO) of P3HT at 5.1 eV. The injected holes can pass through the openings on Al grid and finally arrive at Al collector as the transistor is on. The lowest unoccupied molecular orbital (LUMO) of P3HT is 3 eV, which is 1.3 eV higher than the Al work function of 4.3 eV to suppress unwanted electron current from Al to P3HT. Two differences between vacuum tube triode and the present polymer space-charge-limited transistor shall be mentioned. First, the carrier is hole in polymer space-charge-limited transistor while the carrier is electron in vacuum tube triode. Second, the carrier injection in polymer space-charge-limited transistor is via Ohmic contact, while in vacuum tube triode it is via thermionic emission of heated cathode. The basic operation principle of the transistor is illustrated in Fig. 1(b). The dotted line is the potential profile along a path passing through the metal grid, while the dash line is the profile along a path through the opening. As the transistor is off, no hole is collected due to the barrier between the emitter and opening. As the transistor is on, there is a SCLC between the emitter and opening.

The device is fabricated on patterned ITO glass substrate cleaned in ultrasonic bath. A layer of 500 Å PEDOT:PSS is spin coated onto ITO as the hole injection layer. After baking in vacuum at 200 °C for 10 min, the substrate is transferred to a glove box. P3HT is spin coated from chloroform solution (1 wt %) on the PEDOT:PSS layer, and then baked at 120 °C for 30 min in vacuum. A spin rinsing[21,22] with xylene is used to remove the remaining soluble part of P3HT, and a thin P3HT layer of about 200 Å is obtained. To fabricate Al grid with openings, polystyrene spheres are used as shadow mask. Ethanol solution (0.1 wt %) of polystyrene spheres with various diameters is spin coated on P3HT, followed by 300 Å Al evaporated as the Al grid. After removing the polystyrene spheres by submerging the sample in ethanol for 20 s with ultrasonic agitation, an Al film with openings at the positions of the spheres is formed. A layer of 450 Å P3HT is then spin coated from xylene solution (1 wt %) on the sample, followed by depositing an Al film of 300 Å to complete the device. Ethanol was used to dilute the polystyrene spheres because its alkyl group improves the adhesion between polymer and polystyrene solution. The device active area is 1 mm^2.

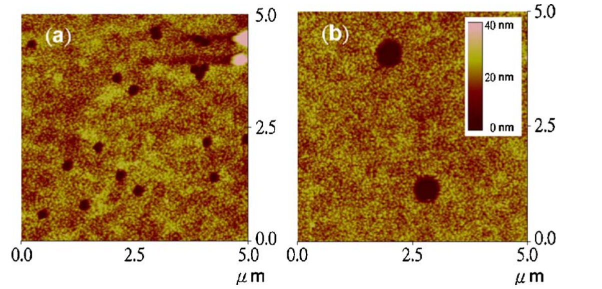

FIG. 2. (Color online) The AFM images of the Al grid after removal of polystyrene spheres with diameter of (a) 2000 Å and (b) 5000 Å. Note the aggregate at the upper right corner of (a).

The AFM images of the surface of Al grid after removal of polystyrene spheres of 2000 and 5000 Å are shown in Figs. 2(a) and 2(b), respectively. The sizes of the openings are almost identical to the diameter of polystyrene spheres, which are removed without causing mechanical damages to the Al grid and the underlying spin-rinsed P3HT film. The spin-rinsed P3HT is intended to provide three advantages. First, the thickness of spin-rinsed P3HT film is usually less than 200 Å, which makes the Al grid much closer to the emitter than the collector. This geometry, similar to the vacuum tube triode, facilitates the Al grid to easily control the potential distribution near the emitter. Second, after the P3HT is spin rinsed with xylene, the film is not easy to be dissolved by xylene in the subsequent processes. This does not only prevent the possible dissolution when spin coating P3HT from xylene on Al grid but also the possible shorting between the emitter and Al grid caused by deformation. Third, the spin-rinsed P3HT film is robust during the removal of polystyrene spheres by ultrasonic agitation.

Figure 3(a) shows the characteristics of polymer space-charge-limited transistor with hole diameter of 2000 Å on Al grid. I_C and V_C are the collector current and voltage, respectively. The ITO electrode is commonly grounded and the Al collector is negatively biased at V_C with respect to ITO. The negative I_C means that holes are driven toward the collector through the grid. The I_C has apparent modulation by the grid voltage V_G. As shown in Fig. 3(b), the grid current I_G is in the order of 10^{-10} A when different V_G are applied. To avoid

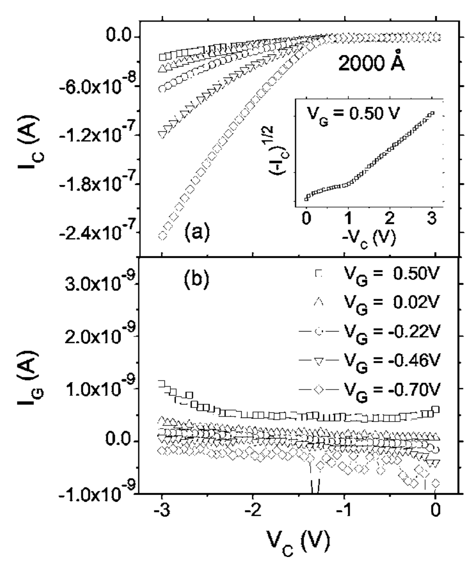

FIG. 3. (a) Collector current I_C and (b) grid current I_G as a function of collector voltage V_C at different grid bias V_G of device with 2000 Å openings on Al grid.

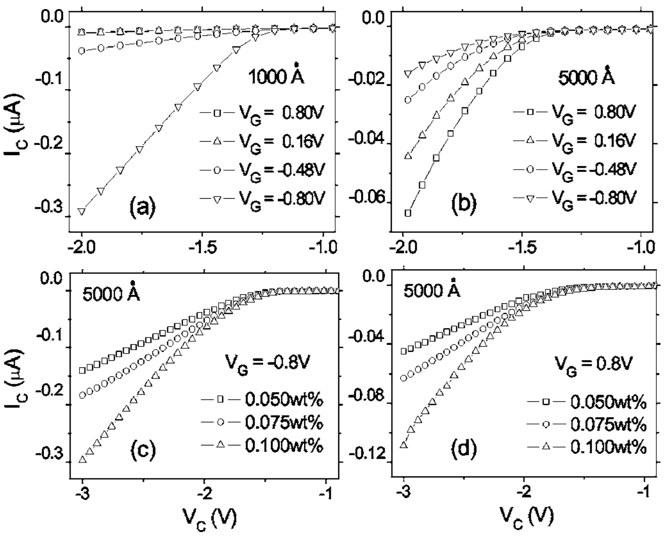

FIG. 4. The characteristics of the polymer space-charge-limited transistor with (a) 1000 Å and (b) 5000 Å opening diameter on Al grid. The characteristics of the polymer space-charge-limited transistor with different concentration of polystyrene spheres used in fabrication process when V_G is (c) −0.8 V and (d) 0.8 V.

large I_G, V_G is restricted to be not more negative than −0.85 V which is the built-in potential between PEDOT:PSS and Al. A large I_G is obtained when negative V_G is applied beyond −0.9 V. The current gain, defined by dI_C/dI_G, is 506 when V_C is −3 V. The transconductance $g_m=(dI_C/dV_G)$ is 3.21×10^{-6} S, calculated from the slope of the I_C-V_G curve in the range from −0.75 to −0.81 V. The off current can be reduced by continuing to increase V_G until the occurrence of a large leakage current between the grid and collector. In principle, lower off current can be achieved by reducing the aggregate of polystyrene spheres, which introduce the big holes on the Al grid film shown in the upper right corner of Fig. 2(a). In order to verify the presumption that this device works in the same way as in vacuum tube triode, we look for signature of the SCLC behavior. The collector current for the vacuum tube triode is given by $I_C=C(\mu V_G+V_C)^n$. μ is the grid amplification factor.[19] The linear combination of grid and collector potential μV_G+V_C is the effective potential at the opening. $n=3/2$ for ballistic SCLC in vacuum and $n=2$ for diffusive SCLC in solid state. Plotting $I_C^{1/2}$ against V_C in the inset of Fig. 3(a) indeed gives a straight line once the barrier at the opening is supressed, confirming the key SCLC presumption. For SIT, I_C would depend exponentially on V_C.[19]

The diameter and density of the openings are also crucial to the properties of polymer space-charge-limited transistor. As demonstrated in Fig. 4(a), the I_C-V_C curves of the device with opening diameter of 1000 Å are overlapped with positive V_G. On the other hand, curves corresponding to the device with opening diameter of 5000 Å separate from each other but with a high off current. The current is difficult to be turned off because of the region around the center of the opening is too far from the Al grid, thus the potential barrier is only enhanced slightly by grid potential ($\mu \ll 1$) before the leakage current between the reverse-biased grid and collector occurrs. Therefore the optimal opening diameter falls in the range of 1000 and 5000 Å. Figures 4(c) and 4(d) show the characteristics of polymer space-charge-limited transistor with different opening density when V_G is −0.8 and 0.8 V. Higher I_C is obtained with higher concentration of polystyrene sphere solution in the fabrication process of Al grid. This indicates that by using the higher concentration of polystyrene sphere solution the higher opening density is obtained, which in turn leads to more current paths and higher I_C. The way to achieve high polystyrene sphere density without aggregation like the case shown in Fig. 2(a) will be the key issue for further study.

In summary, a solution-processed vertical polymer space-charge-limited transistor is demonstrated. A nonlithographic method is introduced for Al grid fabrication with different opening diameters. The operating voltage is as low as 3 V. The transconductance is 3.21×10^{-6} S and the current gain is 506. Such device concept has the potential advantages of easy large-area solution process, high current, low voltage, and being lithography-free.

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