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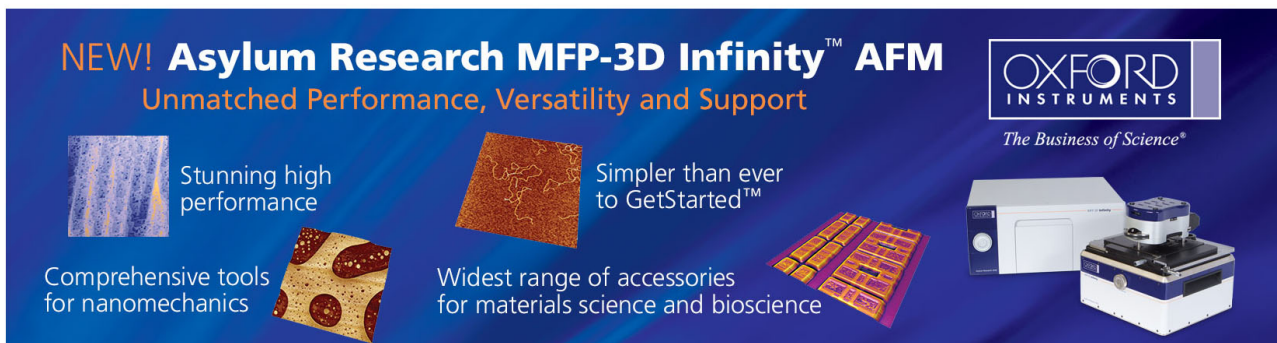
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Reduced hole injection barrier for achieving ultralow voltage polymer space-charge-limited transistor with a high on/off current ratio

Yu-Chiang Chao,¹ Yi-Cheng Lin,¹ Min-Zhi Dai,¹ Hsiao-Wen Zan,^{2,a)} and Hsin-Fei Meng^{1,a)}

¹Institute of Physics, National Chiao Tung University, Hsinchu 300, Taiwan

²Department of Photonics and Institute of Electro-Optical Engineering, National Chiao Tung University, Hsinchu 300, Taiwan

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Vertical polymer space-charge limited transistor (SCLT) operated with an ultralow voltage is demonstrated. The influence of aging effect of the oxygen plasma treated indium tin oxide electrode on the hole injection barrier and on the transistor characteristics is investigated. By reducing the hole injection barrier, the on/off ratio as high as 10^4 is obtained at a collector to emitter voltage as low as -0.84 V. The low operation voltage is crucial to the development of low-power large-area polymer transistor array. Inverter characteristics are also demonstrated by connecting a SCLT with a load resistor. © 2009 American Institute of Physics. [doi:10.1063/1.3261749]

Reducing the operation voltage of transistors is crucial for the development of integrated circuit or large-area transistor array because low operation voltage gives rise to low power consumption. For complementary metal-oxide-semiconductor technology in very-large-scale integration circuits, low operation voltage is achieved by using advanced and expensive lithography processes. For example, $0.18 \mu\text{m}$ process is required to realize metal-oxide-semiconductor field-effect transistors operated by 1 V.¹ For large-area applications, reducing transistor operation voltage by upgrading lithography system to scaling down the channel length is not cost effective. Thin-film transistors (TFTs), such as metal-oxide TFTs,² amorphous silicon TFTs,³ and polycrystalline silicon TFTs,⁴ require operation voltages higher than 5 V. When organic or polymer transistors are considered for the development of printable, flexible, large-area transistor array, operation voltages are even higher than 10 V.

Using vertical-channel transistor structure with ultrashort channel length is an alternative approach to reduce the operation voltage. In previous reports, vertical polymer metal-base transistors with various base conformations have been demonstrated to reduce the operation voltage to be less than 10 V.^{5–8} However, it is important to further reduce the operation voltage to suppress power consumption. Since the vertical channel is a thin polymer semiconductor film sandwiched by two metals (emitter and collector), the thin polymer film gives rise to a low channel resistance while the injection barrier from metal to polymer causes large contact resistance at the metal/polymer interface. When the operation voltage across the vertical channel is reduced, the voltage drop at the metal/polymer interface significantly influences device performance. However, no research has been conducted to understand the influence of hole injection on the characteristics of vertical transistors. Vertical polymer transistor operated with ultralow voltage is still in need. At the same time, low leakage current and high on/off current ratio are required.

In this work, we focus on voltage reduction while keeping on/off current ratio. The vertical transistor we used is space-charge limited transistor (SCLT). The basic concept of

SCLT was proposed and verified in our previous reports,⁸ in which, to operate the transistors, 4 to 7 V across the vertical channel are required. In this work, we reduce the hole injection barrier at indium tin oxide (ITO)/polymer interface. The hole current is enhanced at low voltage. Meanwhile, low electric field suppresses leakage current. The high on/off ratio of 10^4 is obtained at a collector to emitter voltage (V_{CE}) as low as -0.84 V. The characteristics of an inverter fabricated by connecting a SCLT with a resistor in series are also demonstrated.

The structure of the SCLT is shown in Fig. 1(a). The ITO/poly(3-hexylthiophene) (P3HT)/Al diodes are fabricated on ITO glass substrate with or without O_2 plasma treatment on ITO. P3HT of 1200 \AA is spin coated from 2.5 wt % chlorobenzene. To investigate the influence of aging time on the diode characteristics, some ITO glass substrates are stored in glove box for various aging time after O_2 plasma treatment followed by spin coating P3HT. The plasma chamber is connected with glove box such that O_2 -plasma-treated ITO substrates do not contact with ambient air during the investigation of aging time. The SCLT is fabricated on an ITO glass substrate which is flattened by 150 W O_2 plasma for 30 min. 600 \AA cross-linkable poly(4-vinyl phenol) (PVP) is spin coated on the ITO substrate and then cross-linked at 200°C for 60 min in vacuum. Poly(melamine-co-formaldehyde) me-

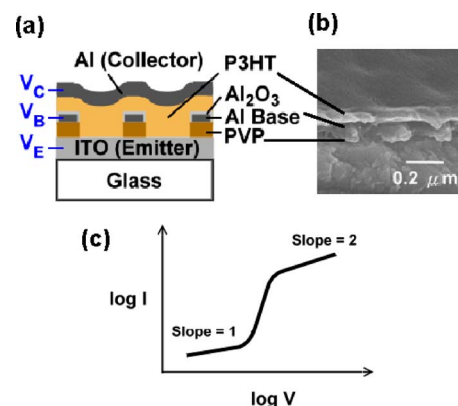


FIG. 1. (Color online) (a) The schematic device structure of a SCLT. (b) SEM image of device before Al collector deposition. (c) The schematic $\log I$ - $\log V$ curve of a SCLT. Three regions with different slopes are observed.

^{a)}Authors to whom correspondence should be addressed. Electronic mail: hsiaowen@mail.nctu.edu.tw and meng@mail.nctu.edu.tw.

thylated (Aldrich, Mw~511) is utilized as a crosslinking agent for PVP. The surface of PVP is turned into hydrophilic by short time exposure of 50 W O₂ plasma before submerging the substrate into 2000 Å positively charged polystyrene spheres (Merck, K6-020) dilute ethanol solution with 0.8 wt %. The polystyrene spheres are adsorbed on PVP surface to serve as the shadow mask. After being submerged in polystyrene spheres solution for 3 min, the substrate is then transferred into a beaker with boiling isopropanol solution for 10 s. The substrate is immediately blown dry to form two dimensional colloidal arrays. 400 Å Al is evaporated as metal base electrode. After removing the polystyrene spheres by an adhesive tape (Scotch, 3M), the PVP at sites without Al coverage is removed by 10 min 150 W O₂ plasma treatment. During the O₂ plasma treatment, Al₂O₃ is also grown on the Al base. The substrate is then stored in glove box for various time before spin coating P3HT of 1200 Å from 2.5 wt % chlorobenzene. Finally, the Al collector is deposited to complete the SCLT with active area as 1 mm². The scanning electron microscopy (SEM) image of device before Al deposition is shown in Fig. 1(b). When SCLT is turned on, the relationship between the channel current (I_C) and the channel voltage (V_{CE}) can be observed by $\log I_C - \log V_{CE}$ curve as shown in Fig. 1(c). The region with a slope equal to 2 refers that the current is the space-charge limited current. When the slope is equal to 1, the conduction is related to the intrinsic carrier density since hole injection is blocked by the interface barrier.⁹ Reducing injection barrier is the key to obtaining high current under low voltage.

Hole injection from ITO has been enhanced by many methods including UV/ozone and plasma treatment. In this work, before spin coating P3HT, the surface of ITO emitter is treated with O₂ plasma during the plasma etch back process. As a result, hole injection from ITO to P3HT is improved by O₂ plasma treatment. The normalized current-voltage curves of ITO/P3HT/Al diodes are shown in Fig. 2(a). The normalized current turns on rapidly at low voltage for the diode fabricated on O₂-plasma-treated ITO. As for the diode fabricated on ITO without O₂ plasma treatment, the normalized current turns on at around 1 V. Previous reports have demonstrated that the changes in surface chemical composition, surface species and surface carbon contribute to the enhanced ITO work function.¹⁰⁻¹² The enhanced ITO work function gives rise to the reduced energy barrier at the interface of ITO and P3HT as shown in the inset of Fig. 2(a). For the diode with low hole injection barrier, hole injection occurs at low voltage and hence the turn-on voltage is low. As for the diode with high-injection barrier, high voltage is needed for hole tunneling through the barrier. Since the enhanced ITO work function is related to the change of surface carbon and surface species, aging effect is expected to significantly influence ITO work function. As shown in Fig. 2(b), aging effect on the O₂-plasma-treated ITO is investigated. Since 2 min are necessary for transferring sample from plasma chamber into glove box and spin coating P3HT, the minimum aging time is estimated as 2 min. Longer aging time is achieved by store sample in glove box for various period of time. For the diode with 2 min aging time, a rapidly increasing current is observed when the forward-bias voltage is applied. However, as the aging time increases from 2 to 62 min, the turn-on voltage of ITO/P3HT/Al diode is increased. In the mean time, the contact angle also rises with

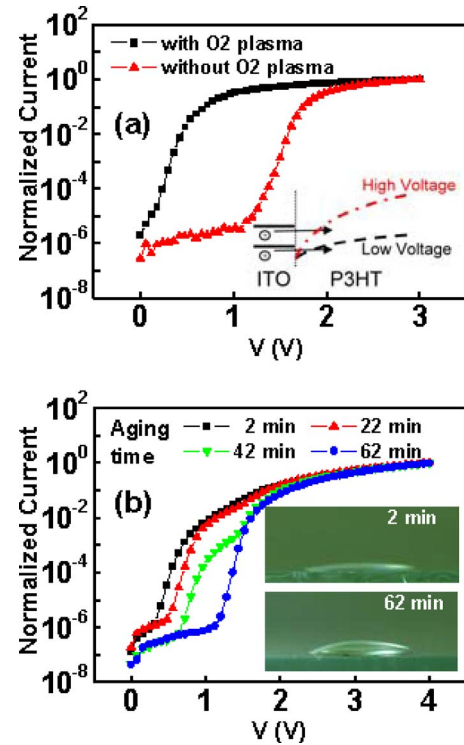


FIG. 2. (Color online) (a) The normalized current-voltage curves of the ITO/P3HT/Al diodes. The ITO surface is treated with or without O₂ plasma. The inset shows the schematic energy level diagrams under low and high voltage. The black solid lines represent the Fermi level of ITO with low and high voltage bias. The black dashed line represents the highest occupied molecular orbital of P3HT while device is under low voltage bias. The red dot-dashed line represents the highest occupied molecular orbital of P3HT while device is under high voltage bias. (b) The normalized current-voltage curves of the diodes fabricated on ITO substrate with different aging time. Images of water drop on ITO surface with aging time of 2 and 62 min are compared in the inset.

the aging time as shown in the inset of Fig. 2(b). Aging time longer than 62 min causes no apparent change on turn-on voltage and contact angle. The observation can be explained as follow. With the increasing aging time, the surface oxygen concentration decreases and the surface carbon concentration increases, which results in the decrement of ITO work function, and thus increment of hole injection barrier as well as turn-on voltage.¹³ After 62 min aging time, the surface condition goes back to that before O₂ plasma treatment, and the benefit brought by O₂ plasma treatment disappeared.

After knowing that O₂ plasma treatment decreases the turn-on voltage and enhances the hole current at low voltage while the aging causes the opposite effect, the influence of the O₂ plasma treatment and the aging effect on the SCLT characteristics is then investigated. The characteristics of SCLTs made with aging time of 2 min (low-injection-barrier SCLT) and 62 min (high-injection-barrier SCLT) are compared and shown in Figs. 3(a) and 3(b). The V_{BE} is changed from negative to positive to turn on and turn off the SCLT. The off current is reduced by increasing V_{BE} until leakage current occurs and causes a large base current density (J_B). Apparently, the collector current density (J_C) can be modulated by V_{BE} for both SCLT. However, the low-injection-barrier SCLT can be turned on at low voltage ($V_{CE} = -0.3$ V) but the high-injection-barrier SCLT can only be turned on with higher voltage ($V_{CE} = -1$ V). This agrees with the results obtained from Fig. 2. Low-injection-barrier SCLT

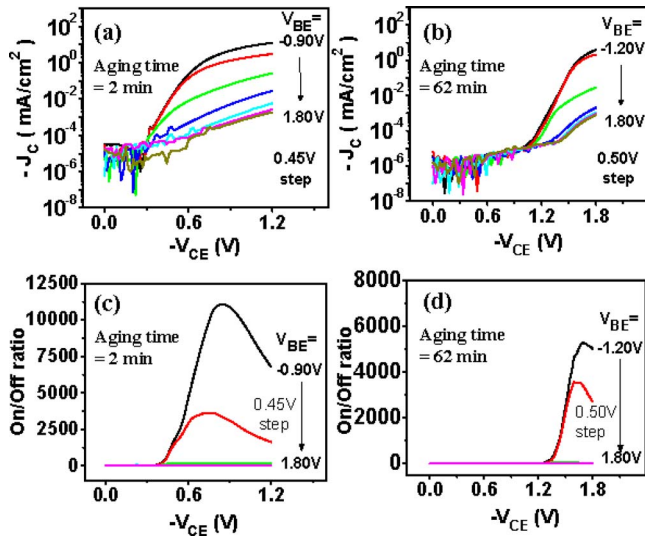


FIG. 3. (Color online) The characteristics of SCLTs made with aging time of (a) 2 min and (b) 62 min. The on/off ratio of SCLTs made with aging time of (c) 2 min and (d) 62 min.

shows good transistor characteristics and the output current density is around 12.7 mA/cm^2 as $V_{CE} = -1.2 \text{ V}$. The base current density is in the order of $10^{-4} - 10^{-3} \text{ mA/cm}^2$ and hence the current gain $|J_C/J_B|$ is as large as 10^4 to 10^5 . The on/off ratio for SCLT with low and high injection barrier is plotted as a function of V_{CE} in Figs. 3(c) and 3(d), respectively. High on/off ratio of 10^4 for low-injection-barrier SCLT is obtained at $V_{CE} = -0.84 \text{ V}$ while that for high-injection-barrier SCLT is about 5000 at $V_{CE} = -1.69 \text{ V}$. Even when more negative V_{CE} and V_{BE} are applied on high-injection-barrier SCLT to turn on the emitter-to-collector diode, the on/off ratio is still lower than that of low-injection-barrier SCLT. The lower on/off ratio in high-injection-barrier SCLT results from higher base-collector voltage drop which increases leakage current and hence reduces the on/off ratio. Operating the SCLT under low voltage can prevent leakage current. Low injection barrier from ITO to P3HT is essential to obtain high output current and high on/off ratio at low operation voltage.

After a SCLT with a high on/off ratio operated within ultralow voltage is fabricated, a resistive-load inverter based on SCLT is demonstrated by connecting a SCLT with a load resistor ($R_L = 1 \text{ M}\Omega$) in series. Schematic inverter circuit is shown in the inset of Fig. 4(a). The transfer characteristics at various supply voltage (V_{DD}) are shown in Fig. 4(a). The output voltage (V_{out}) can be expressed by $V_{out} = (V_{DD}R_{EC})/(R_L + R_{EC})$, where R_{EC} is the effective resistance from emitter to collector. When input voltage (V_{in}) applied on base electrode is 1 V (logic “0”), the SCLT is in the off state, R_{EC} is much larger than R_L and the output voltage (V_{out}) approaches V_{DD} . On the contrary, when V_{in} is -1 V (logic “1”), the SCLT is in the on state, R_{EC} is smaller than R_L and V_{out} approaches zero. Ideally, V_{out} should be equal to 0 V as the SCLT is in the on state. However, in our case, V_{out} is not exactly 0 V because R_{EC} in the on state is comparable to R_L . This problem can be solved by further increasing the on current of SCLT or by replacing R_L with an n-type SCLT. The gain values of the inverter are shown in Fig. 4(b). The absolute value of voltage gain is 1.4, implying that this device may be used in logic circuits as subsequent stages.¹⁴

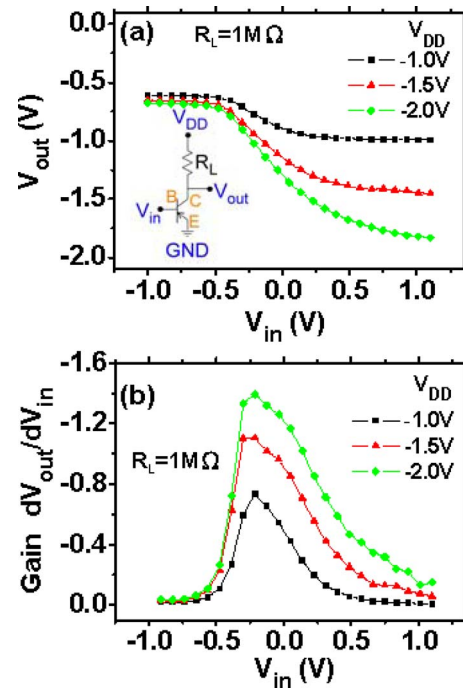


FIG. 4. (Color online) (a) Transfer characteristics of the inverter at various V_{DD} . The schematic inverter circuit is shown in the inset. The load resistance is $1 \text{ M}\Omega$. (b) The corresponding gain values of the inverter.

In summary, the influence of hole injection barrier on the SCLT characteristics is investigated. By fabricating SCLT with minimum aging time after O_2 plasma treatment, the minimum hole injection barrier is obtained, the hole current is enhanced at low voltage, and thus the low operation voltage SCLT is achieved with high on/off ratio of 10^4 at $V_{CE} = -0.84 \text{ V}$. The proposed high on/off ratio and low operation voltage SCLT opens a possibility to develop high-performance organic electronics with large-area solution process. The inverter characteristics represent a promising electronic application with low operation voltage and low power consumption.

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