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Hybrid organic/inorganic ambipolar thin film transistor chemical sensor

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An ambipolar hybrid organic-inorganic thin film transistor, consisting of pentacene and zinc oxide as semiconductors, is reported. The current-voltage characteristics in different operational modes are studied. The transistor is employed as a chemical vapor sensor, operating at room temperature. In *p*-channel accumulation mode, which is dominated by hole transport, a decrease of current with the introduction of analyte is observed, while in the *n*-channel triode mode, in which the current is predominantly contributed by electron transport, an increase in current with analyte delivery is observed. A qualitative model based on dipole interaction is proposed to explain the sensing activity. © *2011 American Institute of Physics*. [doi:10.1063/1.3583594]

Thin film transistor (TFT) based sensors are promising for sensing chemical and biological species, ionic liquids etc.[1–3] Unique properties of organic semiconductors and their ability to interact with different chemical analytes have been exploited to fabricate TFT sensors that can be operated at room temperature.[4,5] However, an important limitation of organic TFT (OTFT) chemical sensors is that the ordinary bias stress effect (which is a decrease in drain current with time due to charge trapping) in the absence of analytes is indistinguishable from drain current decrease due to analytes. This can greatly reduce the sensitivity of sensors and results in false positives. On the other hand, in inorganic TFT sensors, our previous results show that the drain current increases substantially upon exposure to some analytes under highly saturated vapor condition at room temperature.[6] In organic and inorganic TFT sensors the semiconducting thin film is exposed to the analyte. However, inorganic TFT based sensors possess poor response to ethanol possibly and other polar analytes at low concentration.

In this letter, a hybrid ambipolar transistor structure is proposed as a chemical vapor sensor. This sensor combines the chemical interaction of organic semiconductors with polar analytes with the relative stability of an oxide semiconductor. Zinc oxide (ZnO) and pentacene are used as the component semiconductors in the present study. The device operates in four different modes: *p*-channel accumulation, *n*-channel triode, *n*-channel accumulation, and *p*-channel triode, depending on the drain-source voltage (V_{ds}) and gate voltage (V_g). Of these modes, the *n*-channel triode mode is found to be most stable. The sensing takes place due to the interaction of chemical analytes with the holes in organic semiconductor that leads to a change in electron current in the inorganic semiconductor, thereby changing drain current (I_d). This mechanism will be described in detail in the following paragraphs. The sensing activity in *p*-channel accumulation mode, which is dominated by the hole transport in organic semiconductor, resembles the typical OTFT sensor.

The hybrid ambipolar transistor structure, as shown in Fig. 1, was fabricated on an oxidized silicon (Si) substrate. Silicon dioxide (SiO_2) with a thickness of 150 nm was thermally grown on heavily n^+ doped Si (100) substrate using wet oxidation method. The substrates were cleaned using ultrasonification in acetone, isopropyl alcohol, and deionized (DI) water for 5 min each, followed by drying under a stream of nitrogen prior to deposition. Zinc oxide film of thickness 35 nm was coated on top of SiO_2 using electron beam deposition, followed by thermal annealing at 700 °C for 1 h under oxygen ambient. A layer of aluminum (Al) of thickness ~30 nm, followed by silver (Ag) of thickness ~30 nm was thermally evaporated through a shadow mask on top of the oxide semiconductor to define source and drain contacts. Finally, a layer of pentacene (thickness ~35 nm) was sublimed in a thermal evaporator with deposition rate 0.1 Å/s. The transistor characteristics were measured using a HP4155C semiconductor parameter analyzer. The analyte (ethanol) was delivered to the channel region through a syringe using a peristaltic pump together with a valve to control the flow of analyte.[4] All the measurements were carried out at room temperature.

The I_d-V_{ds} and I_d-V_g characteristics for $V_{ds} \geq 0$ are shown in Figs. 2(a) and 2(b), respectively. The drain current characteristic exhibits typical *n*-channel accumulation mode operation in the ZnO layer for $V_g > 0$ with distinct linear and saturation regions. However, at low V_g ($V_g \sim 0$), the drain current increases superlinearly with V_{ds} ($V_{ds} > V_g$), showing triode-like behavior [inset of Fig. 2(a)]. This is due to injection of holes in the pentacene layer. Similar characteristics are typically observed in all-organic ambipolar transistors.[7] The triode-like characteristic continues to predominate when the gate voltage is swept in the negative direction, as observed in Fig. 2(b). This may be considered as the hole injection mode, which is comparatively weak. Since the mo-

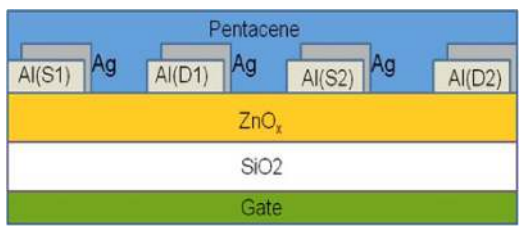

FIG. 1. (Color online) Schematic diagram of ambipolar hybrid organic/inorganic TFTs (dimensions are not scaled).

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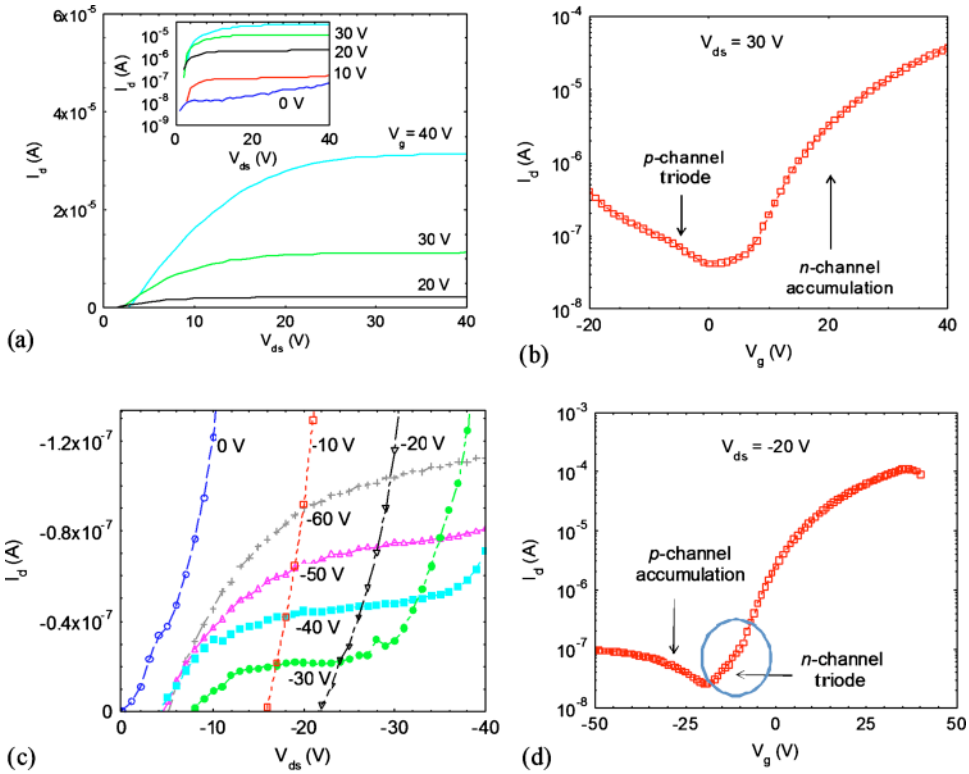

FIG. 2. (Color online) (a) Output and (b) transfer characteristics of hybrid TFTs under $V_{ds}>0$ (n-channel accumulation and p-channel triode modes). Inset of (a) shows output characteristics in semi logarithmic scale. (c) Output and (d) transfer characteristics of the device at $V_{ds}<0$ (p-channel accumulation mode and n-channel triode mode).

bility of electrons in ZnO ($\mu_e \sim 1$ cm^2/V s) is much higher than that of holes in pentacene ($\mu_h \sim 10^{-2}$ cm^2/V s) in our device, electron conduction dominates over hole conduction.

The transistor characteristics remarkably change upon operating the device at V_{ds}, $V_g<0$, as shown in Fig. 2(c). Drain current changes nonlinearly with V_{ds} for negative V_g, showing triode-like behavior. For a fixed V_{ds}, I_d decreases with increase in V_g, which implies that the current is mainly contributed by electrons in ZnO layer. The characteristics start to change at $V_g=-30$ V. The current-voltage characteristic is indicative of hole accumulation behavior under such bias condition together with some triode-like features at $V_{ds}>V_g$. The current increases with the increase in the magnitude of V_g. This is due to normal hole accumulation in the pentacene layer when gate voltage is high enough to induce holes near the pentacene/ZnO interface. The transfer characteristic also shows the transition from p-channel accumulation mode to n-channel triode mode around $V_g \sim -20$ V, as shown in Fig. 2(d).

In order to evaluate the sensing response of the ambipolar device structure, ethanol vapor (2000 ppm) was used as the chemical analyte. The response to the analyte was monitored by detecting the change in drain current during analyte delivery. In p-channel accumulation mode, when the device was operated at $V_{ds}=-20$ V and $V_g=-40$ V, large bias stress effect is observed with a considerable decrease in drain current with time. This is the baseline, as represented by blue line in Fig. 3(a). The large bias stress effect has many possible causes including disorder at the pentacene/ZnO interface. It is also worth mentioning that pentacene is separated from the gate dielectric through the intermediate ZnO layer, which reduces the capacitive effect of gate voltage. The drain current decreases upon analyte delivery at time $t=20$ s, as shown in Fig. 3(a) (red solid line, indicated by arrow). The change is very small against the background of the bias stress effect. The current rises upon terminating analyte delivery at $t=40$ s. The response to chemical analytes was observed to be qualitatively similar to that of OTFT sensor.[5]

The scenario becomes completely different upon operating the device in n-channel triode mode with $V_{ds}=-20$ V and $V_g=-10$ V. Except the initial drop, triode current was observed to be fairly stable with respect to time in the ab-

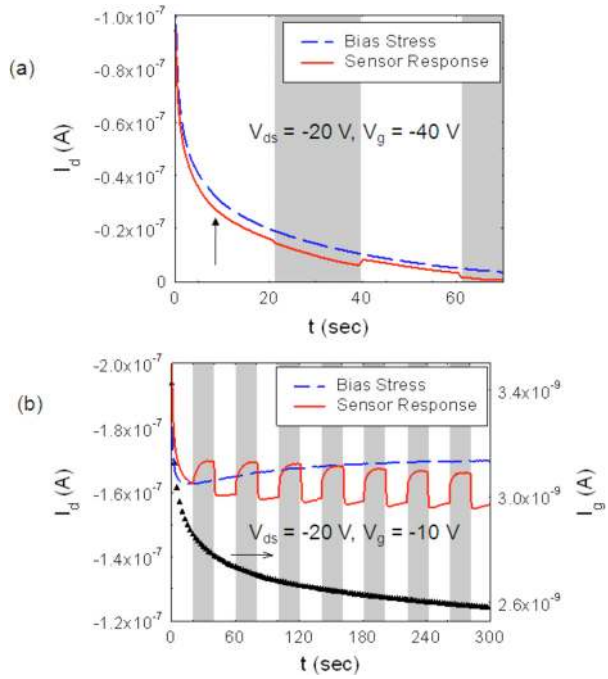

FIG. 3. (Color online) (a) Sensor response of the ambipolar TFT under p-channel accumulation mode (red solid line, indicated by arrow) upon delivering ethanol (shaded region). The blue dashed line represents base line of the sensor, showing large bias stress instability without delivering analyte. (b) Sensor response to ethanol (shaded region) under n-channel triode mode (red solid line). Blue dashed line indicates the base line. The gate leakage current under the influence of ethanol is represented by the black marked line (corresponds to the right axis).

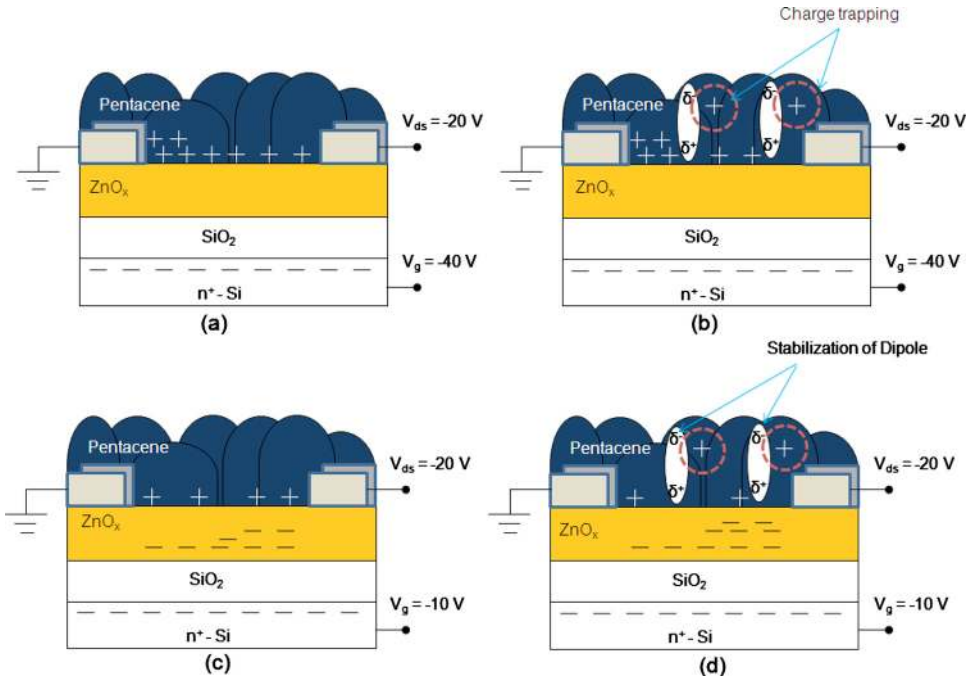

FIG. 4. (Color online) Schematic diagram of proposed mechanism in *p*-channel accumulation mode (a) before and (b) during analyte delivery and in *n*-channel triode mode (a) before and (b) during analyte delivery.

sence of the analyte, as pointed in Fig. 3(b). This flat baseline is beneficial for detecting analyte/sensor responses. Upon delivering the analyte, the current increases from the initial value, while it decreases immediately after terminating the analyte delivery (red solid line). Similar responses were observed repeatedly for several cycles of analyte delivery, as represented by the shaded region in Fig. 3(b). This stable response was reproducible without much change in the baseline (i.e., avoiding bias stress instability) and the gate leakage current [black marked line in Fig. 3(b)]. This is a significant advantage over OTFT sensors, which are typically affected by bias stress problems.

A model, based on the dipole interaction between the analyte molecules and the holes in pentacene is proposed to explain the sensing response of this device structure (Fig. 4). In the *p*-channel accumulation mode, the holes are likely to be induced and distributed near the penatcene/ZnO interface. Upon delivering the analyte, the polar molecules diffuse through the grain boundaries to reach at the pentacene/ZnO interface and trap the holes. As a result, the current is reduced due to the dipole-induced charge trapping process. This process typically occurs in most of the organic semiconductors since the charge transport therein is polaronic that is largely influenced by the presence of polar molecules. In the *n*-channel triode mode, the current is predominantly contributed by the electrons in ZnO. In addition, the presence of holes is still expected in pentacene layer since the bias condition favors the accumulation of holes. Upon introducing the analyte, the polar molecules trap the holes and get stabilized. This is analogous to decreasing the magnitude of the gate bias which results in an increase in drain-source current.

The direct interaction between the analyte molecules and the electrons in the ZnO layer is completely ignored in the preceding model. In order to verify this, a ZnO TFT was fabricated (without Ag and pentacene coating) and tested under the influence of analyte molecules. No significant response was observed upon delivering the analyte. Similarly, the ambipolar device is found to be insensitive to the analyte upon operating in the *n*-channel accumulation mode with $V_{ds}=20$ V and $V_g=30$ V. Introduction of organic semiconductor on top of inorganic semiconductor primarily acts like a receptor with considerable grain boundaries. The stabilization and unidirectional orientation of polar analyte molecules provide an additional top gate effect in the ambipolar TFT sensor.

In conclusion, a hybrid ambipolar transistor sensor that consists of pentacene as a *p*-type organic semiconductor and ZnO as an *n*-type inorganic semiconductor has been demonstrated. The device possesses stable response in the *n*-channel triode mode with an increase in current upon interacting with the analyte. On the other hand, in the *p*-channel accumulation mode, the current decreases upon introducing analyte molecules. A qualitative model based on the dipole interaction between the analyte molecules and the holes is proposed to explain the results. Further understanding of ambipolar sensors and choice of appropriate bilayer structures may lead to the sensors with better stability, sensitivity and selectivity.

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