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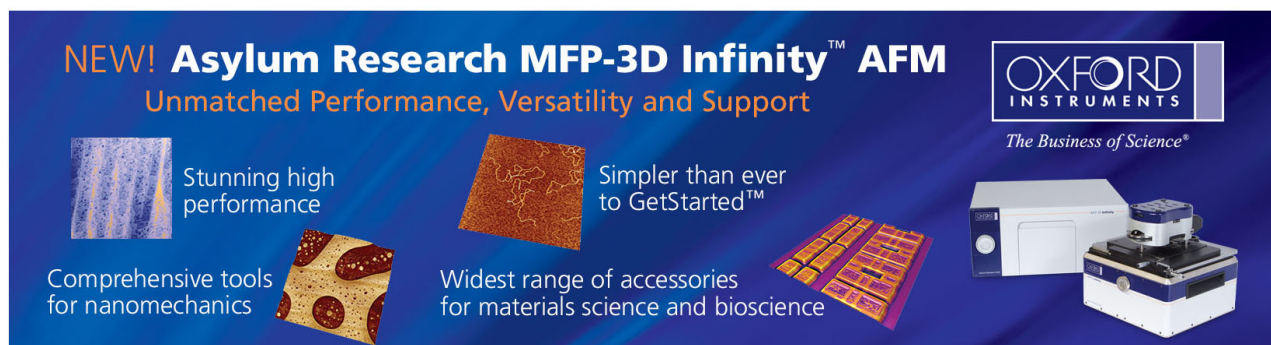
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Room-temperature-operated sensitive hybrid gas sensor based on amorphous indium gallium zinc oxide thin-film transistors

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An organic sensing layer is capped onto an amorphous indium gallium zinc oxide (*a*-IGZO) thin-film transistor (TFT) to form a hybrid sensor. The organic layer, served as a second gate, forms a *p-n* junction with the *a*-IGZO film. Oxidizing or reducing vapor molecules act like electron acceptors or electron donors to change the potential of the organic layer and the current of *a*-IGZO TFT. A sensitive and reversible response to 100 ppb ammonia and 100 ppb acetone is obtained at room temperature. This letter opens a route to develop low-cost large-area bio/chemical sensor arrays based on the emerging *a*-IGZO TFT technology. © 2011 American Institute of Physics. [doi:10.1063/1.3601488]

With a high mobility (>10 cm²/V s), a low threshold voltage (<5 V), a high on/off ratio, high uniformity over large area, and process availability at room temperature, amorphous indium gallium zinc oxide thin-film transistors (*a*-IGZO TFTs) have attracted much attention since they were first reported by Hosono and co-workers.¹ Recently, *a*-IGZO TFTs have been used as the pixel switching or driving circuits in active-matrix liquid crystal displays and active-matrix organic-light-emitting-diode displays.^{2,3} In this letter, we propose a sensitive vapor sensor based on conventional *a*-IGZO TFT. Sensitive vapor sensors are important for the development of noninvasive diagnostic breath analysis system.⁴⁻⁶ For example, the breath NH₃ concentration is higher in patients with liver diseases or disturbed urea balance (~ 0.7 ppm) than that in normal person (<0.3 ppm).⁴ Patients with diabetes exhale higher concentration of acetone than normal persons.⁵ Nitric oxide (NO) gas sensor is important for asthma attack prevention.⁶

However, high sensitivity (<1 ppm) is obtained only when nanostructure is used to increase the surface to volume ratio and the sensors are operated at an elevated temperature (e.g., >200 °C).^{7,8} In this letter, instead of utilizing the reaction between the vapor molecules and the metal-oxide semiconductor material, an organic sensing layer (OSL) is capped onto a conventional bottom-gate top-contact *a*-IGZO TFT to form a hybrid sensor. The organic layer and the *a*-IGZO film form a *p-n* junction. Oxidizing or reducing vapor molecules act like electron acceptors or electron donors to change the potential of the OSL and thus change the energy band equilibrium of the *p-n* junction. As a result, the current of *a*-IGZO TFT is significantly changed. The proposed mechanism has been utilized to form a sensitive visible light sensor in our previous report.⁹ In that work, visible light absorbed by the organic capping layer produces electron-hole pair, injects electrons into *a*-IGZO film, and changes the TFT threshold voltage. In another work, we capped various kinds of metals onto the back interface of *a*-IGZO TFT. The built-in potential between the floating cap-

ping metal and *a*-IGZO is utilized to adjust the device threshold voltage. The capping layer is served as a *floating second gate* to influence the characteristics of *a*-IGZO TFT.¹⁰ In this letter, two kinds of organic materials [poly(3-hexylthiophene) (P3HT) and copper phthalocyanine (CuPc)] are used as the gas sensing layers. The P3HT-capped hybrid sensor and CuPc-capped hybrid sensor exhibit a fast and reversible response to 100 ppb ammonia and 100 ppb acetone, respectively. A gate bias modulated sensitivity is investigated. Opposite responses to electron donors (ammonia and acetone) and electron acceptor (NO) are clearly observed.

First, standard (STD) *a*-IGZO TFTs were fabricated with experimental conditions described in our previous report⁹ while the channel length and width were changed to be 200 μm and 1000 μm , respectively. For P3HT-capped devices, P3HT (RR $>98.5\%$, Rieke Metals Inc.) derived from chlorobenzene (1.5 wt %) was coated on some STD devices in 7000 rpm; the coated devices were then annealed at 200 °C for 10 min. The thickness of the P3HT film was 20 nm. For CuPc-capped devices, a 50-nm-thick CuPc (purity $>99\%$, Lumtec) was deposited on the STD device by thermal evaporation at room temperature with a deposition rate as 0.5 Å/s under 2×10^{-6} torr. The threshold voltage and mobility were determined from the slope and the *x*-axis intercept of the transfer characteristics measured under saturation condition ($V_{DS} = 20$ V; V_{GS} was varied from -15 to 20 V). To investigate the gas sensing response, devices were put in a microfluid sensing chamber and the background ambient is kept as high purity 99.9999% nitrogen (N₂). We used the electrical syringe pump system to inject the test gas (acetone with a purity as 99.999% and NH₃ with a purity as 99.9999%) into a tube to blend with N₂ completely and then the mixed gas enters the microfluid system. The amount of N₂ was controlled by a mass-flow controller and the specific concentration of test gas was attained by adjusting the injection speed of electrical syringe pump. The concentration of NO gas was controlled by a mass-flow controller.

The schematic diagram of organic-capped *a*-IGZO TFT is shown in Fig. 1(a). When the OSL is exposed to oxidizing or reducing gases, the potential of the OSL is changed. Since

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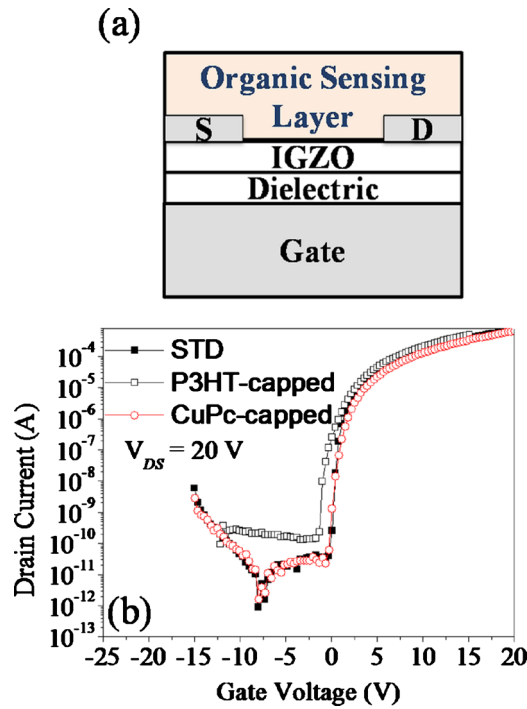


FIG. 1. (Color online) (a) Schematic diagram of organic-capped *a*-IGZO TFT and (b) transfer characteristics of STD, P3HT-capped, and CuPC-capped device measured at $V_{DS}=20$ V.

the OSL is treated as a floating second gate, the potential variation in the OSL significantly influences the current of the *a*-IGZO TFT.

Initial transfer characteristics of STD device, P3HT-capped device, and CuPC-capped device are shown in Fig. 1(b). The field-effect mobilities (μ_{FE}), threshold voltages (V_{TH}), subthreshold swings (S.S.), and on/off ratio of STD device are $13.8 \text{ cm}^2/\text{V s}$, 0.72 V , 0.19 V/dec , and 2.9×10^6 , respectively. For P3HT-capped device, they are $10.7 \text{ cm}^2/\text{V s}$, 1.4 V , 0.28 V/dec , and 2.2×10^6 . For CuPC-capped device, they are $13.3 \text{ cm}^2/\text{V s}$, 1.33 V , 0.27 V/dec , and 1.0×10^7 . Obviously, capping organic semiconductor onto *a*-IGZO TFTs does not cause significant influences on basic device characteristics.

Then, the responses of STD *a*-IGZO TFT and P3HT-capped *a*-IGZO TFT to ammonia are investigated. Drain current variations (ΔI) in these two devices are plotted as a function of time exposed to different ammonia concentration in Fig. 2(a). Devices are biased at $V_{GS}-V_{TH}=0.3 \text{ V}$ and $V_{DS}=1 \text{ V}$. For STD device, no significant response can be observed when ammonia concentration is 10 or 0.8 ppm. For P3HT-capped device, an obvious current drop is obtained when device is exposed to ammonia. After the removal of ammonia, the current drop is recovered. The ammonia sensing response of a P3HT-based organic TFT has been reported with ammonia concentration ranging from 10 to 100 ppm.¹¹ In that report, ammonia molecules behave as acceptorlike deep trap states (or as electron donors) to trap the holes at the P3HT/dielectric interface, shift the threshold voltage to be more negative and cause a current drop. In our study, a positive threshold voltage shift is observed when device is exposed to ammonia (not shown). Ammonia molecules absorbed onto P3HT act like reducing agents to inject electrons into P3HT. The negative potential on P3HT layer, the second gate shifts the threshold voltage to be more positive and

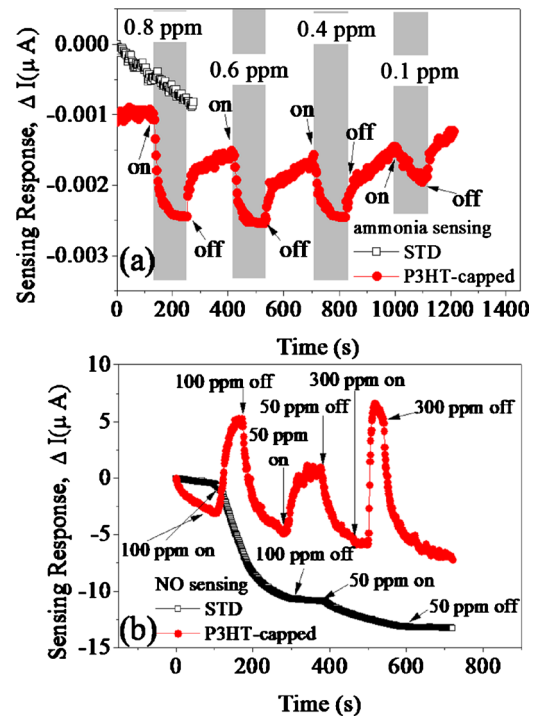


FIG. 2. (Color online) Drain current variation (ΔI) in STD and P3HT-capped device as a function of time exposed to different concentration of (a) ammonia at $V_{GS}-V_{TH}=0.3 \text{ V}$, $V_{DS}=1 \text{ V}$ and (b) NO at $V_{GS}-V_{TH}=8.6 \text{ V}$, $V_{DS}=20 \text{ V}$.

produces a current drop in *a*-IGZO TFT. The sensing sensitivity is high because the threshold voltage is sensitive to the body potential. In our letter, a clear response to 0.1 ppm ammonia is observed. The sensing sensitivity is also strongly influenced by the thickness of P3HT.

To further verify the aforementioned mechanism, a typical oxidizing gas, NO, is used to stimulate the P3HT-capped device. Drain current variations (ΔI) in STD device and of P3HT-capped device are plotted as a function of time exposed to different NO concentration in Fig. 2(b). Devices are biased at $V_{GS}-V_{TH}=8.6 \text{ V}$ and $V_{DS}=20 \text{ V}$. When STD device is exposed to NO gas, a slow current drop is observed. The current drop is not able to be recovered even when NO is removed. The slow and irreversible response is due to the slow adsorption and desorption of NO molecules on the oxide semiconductor thin film.⁶ When P3HT-capped *a*-IGZO TFT is exposed to NO, on the contrary, a fast current increase is observed. A fast recovery behavior is also obtained when NO is removed. The P3HT capping blocks the reaction between NO and *a*-IGZO film. The sensing behavior is dominated by the reaction between NO and P3HT in which NO molecules act as oxidizing agents to withdraw electrons from P3HT.¹² The positive potential on P3HT film helps to turn on the transistor and thus increase the current of *a*-IGZO TFT.

Metal phthalocyanine thin films are also known to be good gas sensors because their electronic properties are affected by the adsorption of oxidation or reducing gas.¹³ In the following section, CuPc is capped onto the back channel of *a*-IGZO TFT to detect a kind of reducing gas, acetone, which is an index gas in the breath of patients with metabolic disease such as diabetes mellitus.⁵ Drain current variations (ΔI) in STD device and CuPC-capped device are plotted as a function of time exposed to different acetone concentration

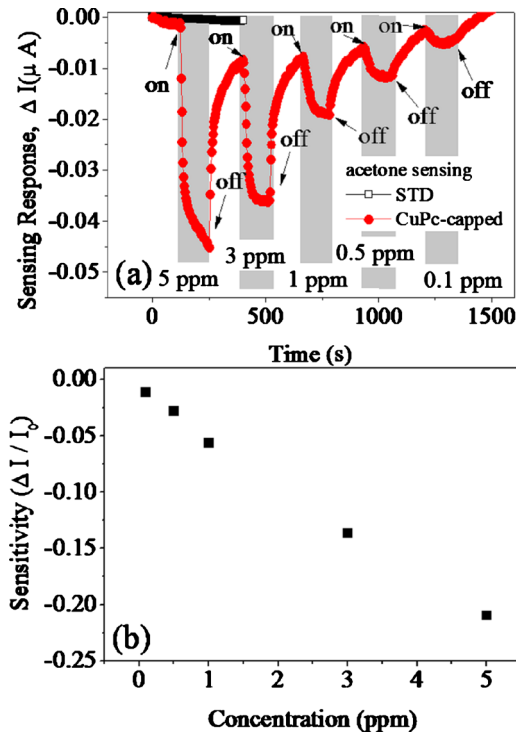


FIG. 3. (Color online) (a) Drain current variations (ΔI) in STD and CuPc-capped device as a function of time exposed to acetone with different concentration at $V_{GS}-V_{TH}=0.5$ V and $V_{DS}=1$ V, (b) the sensitivity (i.e., the current variation ratio, $\Delta I/I_0$) of CuPc-capped device as a function of acetone concentration. Bias conditions: $V_{GS}-V_{TH}=0.5$ V and $V_{DS}=1$ V.

in Fig. 3(a). Devices are biased at $V_{GS}-V_{TH}=0.5$ V and $V_{DS}=1$ V. For STD device, no clear response to acetone can be observed, indicating a weak charge transfer interaction between the *a*-IGZO and acetone at room temperature. For CuPC-capped *a*-IGZO TFT, on the contrary, a fast, sensitive, and reversible response to acetone is obtained. The sensitivity (i.e., the response current variation ratio, $\Delta I/I_0$, when sensing time is fixed as 120 s) is plotted as a function of acetone concentration in Fig. 3(b). A linear relationship is observed. The sensing sensitivity is as high as 100 ppb and is promising to be used to distinguish healthy humans (≤ 900 ppb) and diabetes patients (≥ 1800 ppb). For P3HT-capped device, a linear relationship is also observed when the response current variation ratio is plotted as a function of ammonia concentration (not shown).

An interesting gate-bias-dependent sensing sensitivity is also found. As shown in Fig. 4, the current variation ratio ($\Delta I/I_0$) is plotted as a function of time when devices are

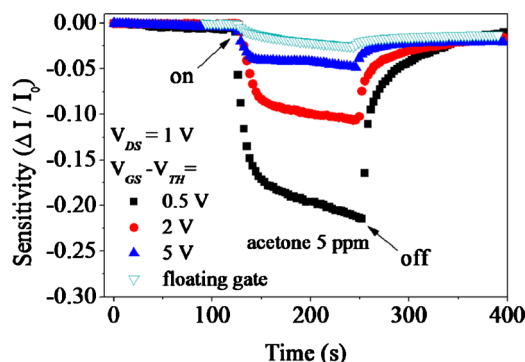


FIG. 4. (Color online) The sensitivity of CuPc-capped device as a function of time exposed to 5 ppm acetone at $V_{DS}=1$ V with different $V_{GS}-V_{TH}$.

exposed to 5 ppm acetone and recovered in pure nitrogen under different bias condition. When $V_{GS}-V_{TH}=5$ V and $V_{DS}=1$ V, $\Delta I/I_0$ is less than 0.04 and is similar to $\Delta I/I_0$ of the floating gate condition, implying that the sensing mechanism is similar to a chemical resistor rather than a chemical transistor. When $V_{GS}-V_{TH}=0.5$ V and $V_{DS}=1$ V, $\Delta I/I_0$ is improved 5.5 times and reaches 0.22. The gate-bias-dependent sensitivity can be explained as follows. When V_{GS} is large, the channel carriers are mostly induced and controlled by V_{GS} . The potential variation in the OSL (i.e., the second gate) caused by the charge transfer between acetone and the OSL is much smaller than V_{GS} . Thus, the channel current has only a weak response to the acetone molecules. When $V_{GS}-V_{TH}=0.5$ V, the potential variation in the OSL is comparable to $V_{GS}-V_{TH}$. The channel current is then significantly influenced by the charge transfer between the OSL and gas molecules.

In this letter, we demonstrated a sensitive gas sensor based on a hybrid organic/inorganic TFT. The OSL is capped onto the back channel of a conventional bottom-gate top-contact *a*-IGZO TFT. When the sensing layer contacts with oxidizing or reducing gas molecules, charge transfer between the sensing layer and the gas molecules changes the potential of the sensing layer. The variation in the sensing layer potential can be detected by the underlying *a*-IGZO TFT since the sensing layer is served as a floating second gate. The organic semiconductor material easily reacts with bio/chemical molecules to cause the charge transfer. The charge transfer is then amplified by the underlying transistor and the sensing current is delivered by the channel in *a*-IGZO film with high electron mobility. The demonstrated sensitivity to 100 ppb acetone and 100 ppb ammonia enables the device to be developed for noninvasive diagnostic of patients with diabetes or liver diseases.

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