

Dual Gate Architecture for High Sensitivity, High Selectivity Chemical-Sensing Field Effect Transistors

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Abstract—Field effect transistors have been pursued as chemical sensors for decades because of their high sensitivity. These sensors generally fall into two categories depending on where the sensing takes place. In the “sensing semiconductor” type, the semiconducting layer is responsible for detecting the analyte. The gate electrode is isolated from the environment and a potential is applied to drive the transistor into saturation. While this configuration offers exception sensitivity, selectivity is poor. Furthermore, the detection layer must also have the ability to conduct, limiting the number of materials that can be used. This is particularly problematic for organic materials, which generally offer superior selectivity through molecular design. The other configuration, “sensing gate”, switches the positions of the gate electrode and the semiconductor so that the gate is in contact with the analyte and the semiconductor is isolated from the environment. The gate is functionalized to be sensitive to a particular analyte, which improves selectivity. However, without the ability to drive the transistor into saturation, sensitivity is tends to be poor. In this work, a dual gate field effect transistor (DG-FET) is introduced. A top gate functionalized for sensitivity to ammonia is responsible for interacting with the analyte. A second gate on the bottom of the device is used to drive the transistor into saturation to provide the sensitivity enhancement. With this configuration, the high sensitivity of the sensing semiconductor configuration is obtained in parallel with the superior selectivity of the sensing gate architecture.

I. INTRODUCTION

Chemical-sensing field effect transistors (chemFETs) have been pursued for decades because of their enticing potential for high sensitivity [1]. The expectation of high sensitivity stems from the non-linear characteristics of transistors. When the transistor is saturated, its drain-source current is proportional to the square of the gate voltage, which can be used to amplify signals including those provided by low concentration chemical species. In spite of nearly 40 years of chemFET research [2], practical devices have yet to be produced. Indeed, chemFETs have been hindered by either poor selectivity or low sensitivity, depending on the configuration.

In the more traditional configuration, the semiconductor layer is exposed to the analyte (the “sensing semiconductor” or SS-FET). The gate electrode is used to drive the transistor to saturation, which provides enhanced sensitivity [3]. The SS-FET is highly sensitive due to its high gain, achieving detection limits in the parts per billion range [4], [5]. Unfortunately, this configuration has very poor selectivity due to the variety of mechanisms that are able to cause a change in signal [6]. The analyte can dope the semiconductor through charge transfer,

introduce trap states if it can diffuse into the semiconductor to the dielectric interface, or cause the semiconducting layer to swell, changing its conductivity [7]. The selectivity issue is what kept this breed of chemFET sensor from real world implementation.

The other configuration, referred to as “sensing gate” or SG-FET, offers improved selectivity [8]. In this case, the structure is inverted compared to the SS-FET. The semiconductor layer is protected from the environment by the gate electrode and dielectric. A functional material is applied to the gate electrode to enhance interaction with the target analyte, thereby improving selectivity over the SS-FET. Rather than the variety of mechanisms that can trigger the SS-FET sensor, the SG-FET only reads charge transfer events (i.e., a change in the work function of the gate electrode) [9]. Limiting the detection mechanisms further improves selectivity. Additionally, because the functional layer does not need to be conductive, a wider variety of sensing materials can be used [10]. The improvements come at the expense of sensitivity. Organic field effect transistors generally feature large threshold voltages due to an abundance of trap states that must be filled [11]. Essentially, this means the gate electrode must accumulate a large amount of material before a signal is observed because it must overcome the threshold voltage for a significant current to flow.

Recently, it was shown that the threshold voltage of a field effect transistor can be modulated with the addition of a second gate. The resulting device looks like a combination of the two types of chemFET described above: a semiconductor sandwiched between two dielectric layer and two gate electrodes. Generally, the top gate is used to control the threshold voltage of the bottom gate due to the surface roughness of the semiconductor [12]. Small molecule semiconductors, such as pentacene, have been used extensively because of their relatively high charge carrier mobility, but the roughness of films of these materials prevents a conduction channel from forming along the top interface [13]. While this technique was effective in creating a microprocessor [14] and other integrated circuits [15], [16] based on organic semiconductors by controlling the threshold voltage, its performance in sensor applications has left much to be desired. Typically, the reported signal is a shift in threshold voltage on the bottom gate caused by charge on the top gate electrode. Obtaining the threshold voltage shift requires a sweep of the bottom gate and calculation, so measurements cannot be performed in real time. It is more desirable to measure the drain current because

it can be measured directly. However, unless a channel is able to form at the top dielectric/semiconductor interface, the drain current will not change much in the presence of an analyte. The quality of this interface is the main factor limiting the performance of this type of transistor-based sensor.

Semiconducting polymers offer smoother surfaces, which have enabled high performance conduction pathways along the top interface [17], [18]. In fact, dual-gate field effect transistors (DG-FETs) utilizing polymer semiconductors have been demonstrated with essentially equivalent charge carrier mobility at both interfaces [19], [20]. Importantly, these materials have experienced a sharp improvement over the past few years, with charge carrier mobilities now rivaling those of their small molecule cousins. This is important for sensors because current is proportional to mobility, so a high mobility leads to a larger signal [21]. To date, no reports of sensors using DG-FETs featuring high mobility ($> 0.1 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) polymer semiconductors could be found.

In this work, a sensor for ammonia is demonstrated using DG-FET architecture. Unlike previous DG-FET designs, our use of the polymer enables us to monitor the channel formed at the top interface which provides a more direct measurement of presence of the desired analyte. We present an enhanced sensor response (over four orders of magnitude) over the sensing-gate configuration. The measurement was taken in real time through drain-source current measurement and the observed response occurs within one second of exposure.

II. EXPERIMENTAL

Interdigitated electrodes (10 nm Ti, 70 nm Au) were fabricated using lift-off lithography on a heavily-doped n-type Silicon substrate with 300 nm of thermal oxide. The electrodes featured a 75 μm width and a 20 μm gap. The chips were washed by 30 of sonication in acetone, methanol, propanol, and toluene and left overnight in octadecyltrichlorosilane (75 mM, toluene). The surface treatment left the surface hydrophobic, which improved the adhesion of the semiconduct-

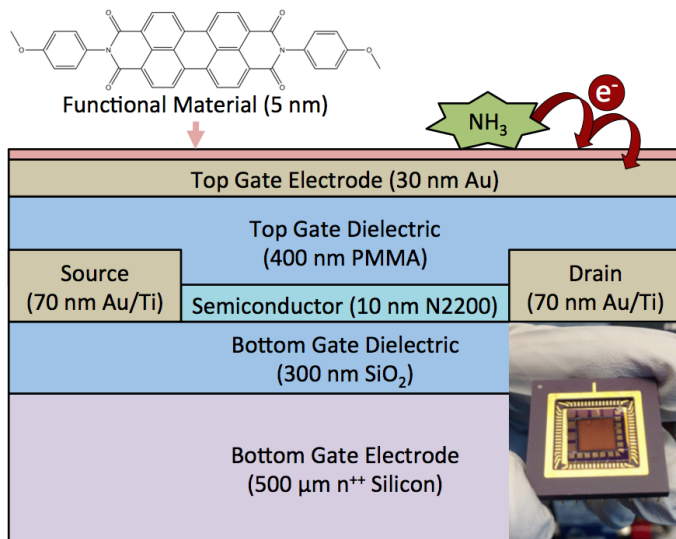


Fig. 1. Molecular structure of the material used for gate functionalization with a schematic (not to scale) and photograph of the sensor (inset).

ing polymer layer. The chips were sonicated once more in toluene, acetone, methanol, and propanol (30 s each), then dried with nitrogen and baked at 110 °C for five minutes. Polyera ActivInk N2200 (5 mg/mL, dichlorobenzene) was spin cast at 2000 rpm for 30 s, followed by one hour of drying at 110 °C in a vacuum oven. This material is an n-type polymer with a mobility of $0.85 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ [22]. The top dielectric, PMMA (75 mg/mL, ethyl acetate), was then spin cast at 2000 rpm for 30 s and dried for thirty minutes at 60 °C in a vacuum oven. The gold top gate electrode (30 nm) was then deposited by thermal evaporation. Finally, the functional material, bis-methoxyphenol-perylene tetracarboxylic diimide (5 nm) was deposited by thermal evaporation. A scheme and photograph of the device are shown in Figure 1.

The film thicknesses were measured with atomic force microscopy (ca. 10 nm for N2200 and ca. 400 nm for PMMA). The rms roughness of the N2200 film matched that of the SiO_2 substrate at 0.6 nm, which enables conduction channel formation along the interface nearest the sensing gate. These measurements were taken with a Veeco MultiMode V microscope. All electrical measurements were taken with an Agilent 4156C semiconductor analyzer in the dark under ambient conditions. The analyte was introduced through a syringe filled with air from the headspace of a bottle containing ammonia.

III. RESULTS

The operation of the DG-FET as a sensor utilizes the bottom gate to modulate the threshold voltage of the top gate. The bottom gate is used to drive the top gate into saturation prior to exposure. Then, when a charge transfer event occurs between the analyte and top gate electrode, the electrode's work function changes. A change in the work function produces a change in current along the top conduction pathway. Therefore, conductivity along the top dielectric/semiconductor interface is

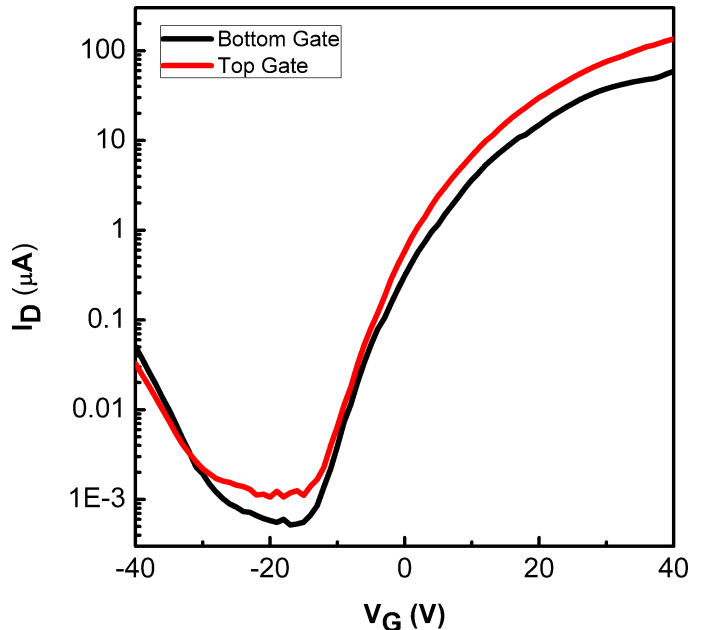


Fig. 2. The transfer characteristics of the transistors operated by the top and bottom gate electrodes. Data were collected from the same device. In both cases, the unused gate was left floating.

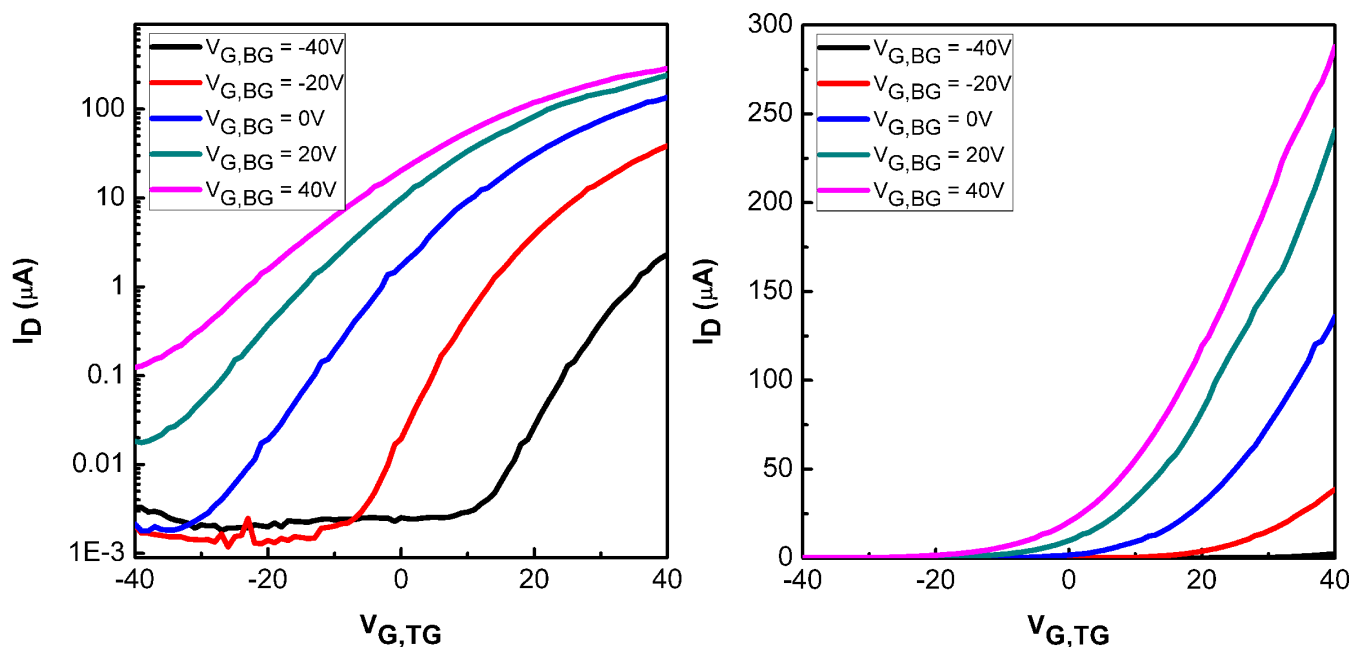


Fig. 3. The transfer characteristic of the DG-FET when a constant voltage is applied to the bottom gate on a logarithmic (left) and linear scale (right).

essential. To confirm this, a voltage was applied to the top gate and swept from -40 to 40 V. A bias of 40 V was applied to the drain. The desired channel indeed formed. In fact, conduction along the top dielectric/semiconductor interface was slightly better than at the bottom dielectric/semiconductor interface using the same test conditions (Figure 2). With the conduction pathway demonstrated, the ability of the bottom gate to modulate the top gate's threshold voltage was investigated next. The bottom gate was fixed at voltages ranging from -40 to 40 V with a step size of 20 V while the top gate was swept from -40 to 40 V as before (Figure 3).

From the transfer characteristics, two features are apparent. First, a positive voltage applied to the bottom gate causes a negative shift in the threshold voltage of the top gate. This is an effect of the small thickness of the semiconducting layer. The depletion width is greater than the thickness of the semiconductor, so the volume of electrons accumulated at the bottom dielectric/semiconductor interface spans the entire layer and increases the electron density at the top dielectric/semiconductor interface. The increased number of electrons at this interface changes the threshold voltage by reducing the number of electrons that must be accumulated by the top gate. Also noteworthy is the increased off current when the bottom gate has a positive voltage. The off current likely originates from charge accumulation at the bottom dielectric/semiconductor interface. This accumulation causes the formation of channel and a current is able to flow. It is important to manage the off current because it might be a limiting factor of the magnitude of a sensor. Here, the on/off ratio is still over 1000 , so this issue is avoided. It might be possible to prevent conduction from occurring by introducing traps at the bottom dielectric/semiconductor interface.

To demonstrate the advantageousness of our device over the traditional sensing-gate FET, the responses of the DG-FET with or without 40 V applied to the control gate. The latter was

used as a control because it is essentially a SG-FET. The same device was used for both configurations, as the sensor is able to recover after one hour in a vacuum oven at 50 °C. In both cases, the drain-source voltage was set to 40 V. Upon exposure to a saturated vapor of ammonia, both showed a rapid response (< 1 s for a 90% change) and a reduction in current exceeding 99% overall (Figure 4). Notably, the decrease in current also confirms the detection mechanism is due to charge transfer. Since ammonia is an electron donor, exposure to the analyte is expected to apply a negative charge to the top gate electrode.

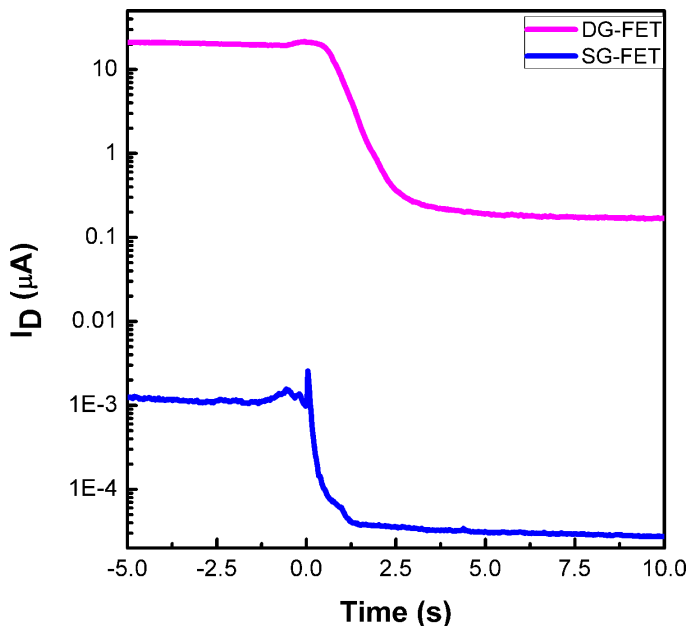


Fig. 4. A comparison between the DG-FET and traditional SG-FET. When exposed to a saturated vapor of ammonia, the DG-FET shows a response four orders of magnitude larger than the SG-FET. The exposure occurs at $t = 0$ s.

This will decrease the current. If ammonia molecules were diffusing into the semiconductor, they would dope the N2200 film. Because N2200 is an n-type polymer, the result would be an increase in current. This confirms that the mechanism is the same as in the SG-FET, as expected. Thus, we anticipate the same selectivity advantages of the SG-FET, although further work is required to verify this claim.

The main advantage of the DG-FET is the larger signal it provides. The current is over four orders of magnitude larger than that measured in the SG-FET with the same relative response (ca. 100). This shows that for the same noise floor, the signal to noise ratio is over four times larger in the DG-FET. Thus, the DG-FET is expected to provide higher sensitivity with fewer false positives. A limit of detection comparison is currently underway. Alternatively, if a large signal is not required (e.g., for monitoring chemicals that do not require high sensitivity), the DG-FET can reduce power consumption by providing a signal equivalent to the SG-FET but requiring lower voltages. Further work in these areas is underway.

IV. CONCLUSION

Field effect transistors are strong candidates for next generation chemical sensors. While chemFETs have been pursued for decades, there are still challenges to overcome. The SS-FET is very sensitive, but suffers from a lack of sensitivity. It also requires the sensing material to have the ability to conduct. The SG-FET provides selectivity, but at the expense of sensitivity. The conductivity requirement is also removed. Neither is sufficient on its own for practical applications.

In this work, we present a DG-FET sensor. Electrical characterization confirms the presence of a conductive pathway along the top dielectric/semiconductor interface. Furthermore, the bottom gate is able to modulate the threshold voltage of the top gate, which drives the transistor into saturation mode, which is ideal for sensing. By doing so, the low sensitivity of the SG-FET is overcome without sacrificing selectivity. Additionally, the measurements occur in real time without the need for extra calculations. As in the SG-FET, the conductivity requirement is not present in the DG-FET, allowing for a wider range of sensing materials to be employed. The selectivity and sensitivity provided by the DG-FET may one day allow the chemFETs to move from the lab to real world implementation.

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