



# Article **TCAD Device Modeling and Simulation Study of Organic Field** Effect Transistor-Based pH Sensor with Tunable Sensitivity for Surpassing Nernst Limit

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Abstract: A dual-gate organic field effect transistor (DG-OFET)-based pH sensor is proposed that will be able to detect the variations in the aqueous (electrolyte) medium. In this structure, a source-sided underlap technique with a dual-gate sensing approach has been used. The change in ON-current (I<sub>ON</sub>) was observed due to parallel examination of electrolytes in two gates underlapping the region of the structure. For the evaluation of the sensitivity of DG-OFET, the change in the drain current was exploited for different pH and corresponding charge densities utilizing 2D physics-based numerical simulation. The simulation results were extracted with the help of the software package Silvaco TCAD-ATLAS. The simulated results display that the proposed DG-OFET shows significantly higher sensitivity for high-k dielectrics. The voltage sensitivity achieved by DG-OFET with SiO<sub>2</sub> as a dielectric in our work is 217.53 mV/pH which surpasses the Nernst Limit nearly four times. However, using a high-k dielectric (Ta<sub>2</sub>O<sub>5</sub>) increases it further to 555.284 mV/pH which is more than nine times the Nernst Limit. The DG-OFET pH sensor has a lot of potential in the future for various flexible sensing applications due to its flexibility, being highly sensitive, biocompatible and low-cost.

Keywords: pH; sensitivity; pentacene; organic FET; electrolyte; Nernst limit

## 1. Introduction

The ion-sensitive field effect transistor (ISFET) is based on inorganic field-effect transistors where an electrolyte solution and an ion-sensitive membrane are embedded. As these devices have many advantages, they show good compatibility with the CMOS technology, control the process very precisely, operate at equilibrium conditions, are capable of showing label-free detection, and are easy to use; yet, these devices suffer from a few innate deficiencies [1]. In the case of long-term use, they are unreliable and unstable due to ionic damage. For sensing purposes, the main principle involves a variation in the surface capacity that occurs due to ionic interactions at the electrolyte/gate oxide. Derived sensing margin in ISFET is the main constraint that lies within the Nernstian limit (59 mV per pH) at room temperature, and this has gained much research attention over the past few decades [2]. Thus, different devices have been tried till now to improve the sensing margin (>59 mV per pH) and hence this results in different device designs with different Configurations [3].

We also proceeded with our work with the same aim to improve the Nernestian limit using an organic field effect transistor as a device, and hence tried different configurations to get the desired results. With the discovery of polymers with high conductivity in the 1970s by Shirakawa et al. [4], much attention has been grabbed by organic field effect transistors (OFETs) [5]. In organic electronics, organic semiconductors have received a lot of attention, and this has proved to be a substitute for conventional inorganic semiconductors [6] due to their economical possessing plasticity, fabricability and large area



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usage [7,8]. A considerable potential application among OFETs is its printability, due to which high density and large circuits can be produced on flexible substrates, and thus, low-cost devices can be possible. A blend of "printed electronics" and "organic transistors" can help in providing low-cost and several functional devices at a large scale [9–11]. To date, amongst the numerous OFETs based on organic semiconductors, pentacene-based OFETs have been confirmed to have the uppermost mobility and adequately high ON/OFF current ratios [12,13]. Most of the reported OFET-based pH sensors in the literature have been fashioned on an architecture similar to ISFETs [14,15]. The electrolyte is responsible for the variation of the carriers within the semiconductor layer and is placed on top of the gate insulator, and to provide effective biasing within the transistor, the Ag/AgCl electrode is submerged in the electrolyte. Numerous studies have been reported where organic semiconductor field-effect transistors (FETs) are used as gas or pH-level sensors. Torsi reported a gas sensor, where the carrier mobility of the organic semiconductor is modulated by a gas interaction with it, which was confirmed by the I–V characteristics of the sensor [16–18]. The ion-selective field effect transistor (ISFET) was employed by Bartic to sense the pH of the solution [14]. Throughout the last few decades, the sensing capability of OFET-based pH sensors have been assessed for optimum device performance [19–21]. Yet, using OTFTs in sensing applications with good sensitivity is still a challenge. The dielectrically modulated pH sensor based on an organic field effect transistor has received comparatively little attention from simulation and modeling perspectives. The main aim of this study was to model and simulate a low-cost, flexible organic-based transistor that monitors the phenomenon occurring at the electrolyte and dielectric interface by assessing the variations in the channel conductivity due to electrolyte solution. Moreover, to achieve better pH sensitivity of a sample solution, a suitable recognition layer is added to the transistor that can provide specificity towards various charged or neutral entities in the solution [14]. Like traditional inorganic chemical sensor-based field effect transistors, the sensing mechanism of an organic-based pH sensor is the same [22]. The change in pH brings a change in the current, which is due to fluctuations in potential across the dielectric and semiconductor interface. Traditional silicon-based ion-sensitive field effect transistors (ISFETs) are developed using CMOS technology. However, in addition to the price of production, the problems with long-term stabilization significantly limit their implementations [23]. Over traditional electronics, organic materials offer reduced processing temperatures and can be used in inexpensive substrates like polymers or glass, and are frequently connected with less expensive processing and, as a result, throwaway goods. Because of the need for safety, disposable devices are widely preferred for applications relating to health.

## 2. Simulation and Setup

The simulation of our device was implemented using an ATLAS (Silvaco) TCAD tool [24]. In order to sense the pH of the electrolyte design of a novel OTFT structure using organic material, Pentacene has been proposed, as shown in Figure 1. The DG-OFET uses double gates to improve sensitivity and performance over a conventional OTFT-based sensor. The structure consists of an aluminium layer with a thickness of 30 nm used as the gate electrode, gate oxide of thickness 3 nm, and underlap region of thickness 50 nm. On top of this oxide layer, a 400 nm-thick organic semiconducting layer of pentacene is deposited and 50 nm-thick patterned source and drain electrodes of gold are used in the device. The gate dielectric SiO<sub>2</sub> is ultra-thin (3 nm) and intended for high capacitance and low voltages, and is sufficient enough to restrict the mobilization of biomolecules or chemical ions. The parameters used in the simulation were calibrated to match the experimental characteristics according to Ref. [25]. Numerous reports on the fabrication of underlap structure-based FET biosensors have been reported [26,27]. The proposed OFET was fabricated on a glass substrate followed by deposition of an organic semiconductor (OSC) Pentacene through thermal evaporation under high-vacuum conditions [28]. Afterward, the distinct gate insulators are deposited on the sample. Moreover, it is followed by metallization of

the source and drain using gold (Au) contacts. Additionally, a Gate electrode metal of aluminum (Al) was deposited on the oxide using RF sputtering, and finally, the cavity for the placement of the electrolyte was created by etching out the oxide from the source side using buffered HF solution [28].



**Figure 1.** Schematic of our proposed dual-gate Pentacene based OFET pH sensor with dual underlap lap region.

In the simulation, the electrolyte is modeled as a semiconductor by making use of the similarity between the Poisson-Boltzmann equation for ions of electrolyte and electronsholes pairs in an intrinsic semiconductor [29–32]. The monovalent electrolyte is also modeled as an intrinsic semiconductor with a zero-energy band gap and permittivity of water (k = 80) [29–32]. The representation of holes and electrons in the semiconductor is done by positive and negative ions of the solution and in order to replicate the behaviour of Na<sup>+</sup> and Cl<sup>-</sup> the maximum value of mobility of Na<sup>+</sup> and Cl<sup>-</sup> for 1 mmol/L concentration of NaCl solution would be  $4.98 \times 10^{-4}$  cm<sup>2</sup>/Vs and  $6.88 \times 10^{-4}$  cm<sup>2</sup>/Vs as per S. Koneshan et al. [33] and these values as the maximum velocity of holes and electrons are used respectively in semiconductors (electrolyte). An electric double-layer model has been included with a thickness of 1 nm and a constant permittivity of 2 in our simulation, as per the Refs. [31,32]. The thickness of the cavity region for electrolytes was taken to be 50 nm. The various models used in our simulation are fldmob and langevin. The Poole–Frenkel mobility model (pfmob) and Langevin recombination models report the transport and recombination mechanism. In order to accurately represent the action in organic materials, these models have utilized transport and recombination mechanisms

within the organic material are accounted for by the Poole–Frenkel mobility model (pfmob) and Langevin recombination models, respectively. For a finite element-based simulation, the Poole–Frenkel mobility model is expressed as given in Equation (1):

$$\mu(\mathbf{E}) = \mu_0 \exp\left[-\frac{\Delta}{kT} + \left(\frac{\beta}{kT} - \gamma\right)\sqrt{E}\right]$$
(1)

where  $\mu(E)$ , *E* and  $\mu_0$ , respectively, stand for field-dependent mobility, electric field, and zero mobility. While  $\Delta$  and  $\beta$  specify the activation energy and hole Poole–Frenkel constant respectively, whereas  $\gamma$  is employed as the fitting parameter. According to many researchers, the activation energy falls between 0.005–0.050 eV [34–37]. For pentacene material, the values of  $\Delta$  and  $\beta$  are taken to be  $1.792 \times 10^{-2}$  eV and  $7.758 \times 10^{-5}$  eV(cm/V)<sup>0.5</sup>, respectively [34]. The Poole–Frenkel mobility model (pfmob) was used for both electrons and holes specifically for organic materials. Charge carrier mobility in the presence of an electric field was taken into account using the field-dependent mobility (fldmob) model and it varies with mobility enhancement factor  $\gamma$ ; as given by Equation (2):

$$\mu = \mu_{0(V_{GS-V_T})} \tag{2}$$

where:

$$\gamma = \frac{\sqrt{2qN_A\varepsilon_{osc}}}{C_i} \tag{3}$$

Hence,  $\mu_0$  is usually taken as band mobility for the material under analysis. When the overdrive gate voltage is lower, it is assumed to be the reference mobility.

The parameter  $\gamma$  is connected to the device's conduction mechanism and is affected by gate capacitance, semiconductor permittivity ( $\varepsilon_{OSC}$ ), and semiconductor doping density ( $N_A$ ). As for both amorphous and nanocrystalline materials, a positive voltage co-efficient of mobility is observed; hence, it is considered positive, that is,  $\gamma > 0$  [38,39]. Langevin was used to capture the recombination effect in organic materials and the langevin recombination rate is mathematically expressed as [40] in Equation (4)

$$R_{Langevin} = \gamma(np - n_i p_i) \tag{4}$$

where n(p) is the free electron (hole) density,  $n_i(p_i)$  is the intrinsic electron (hole) density and  $\gamma$  is the langevin recombination rate constant.

A combination of the Gouy–Chapman–stern model and Site Binding theory defines the relationship between the pH of electrolyte and surface potential ( $\psi_0$ ) and is given as the Ref. [41] mentioned in Equation (5):

$$\frac{d\psi_0}{dpH} = \frac{2.303\alpha kt}{q} \tag{5}$$

where  $\psi_0$  is the surface potential at the oxide/electrolyte interface,  $\alpha$  is the sensitivity parameter whose values vary between 0 and 1 depending on the value of buffer capacitance of gate dielectric and the electrolyte solutions concentration, *k* is Boltzmann's constant, and *t* is temperature.

In an electrolyte solution when the pH is changed, the oxide sensing surface remains in the dynamic protonation and deprotonation state to capture the ions which results in a change in the potential of the electrolyte solution near the oxide surface while keeping the potential at the extreme end equal to the reference bias. Thus, the relationship between surface potential and pH for oxide surface is defined in Equation (6) as in the Ref. [42]:

$$\psi_0 = \frac{1}{\beta} \left[ 2.303 \left( pH_{pzc} - pH \right) - sinh^{-1} \left( \frac{\sigma_0}{2q \left( \frac{K_b}{K_a} \right)^{\frac{1}{2}} N_s} \right) + \ln \left( 1 - \frac{\sigma_0}{qN_s} \right) \right]$$
(6)

where  $\beta$  is a constant that can be calculated by the Gouy–Chapman stern model,  $kt/q = V_{th}$  is thermal voltage (26 mV at room temperature) and  $pH_{pzc}$ ,  $pK_a$  and  $pK_b$  are defined as the dissociation constants where surface charge density is zero and is given by Equations (7)–(9) respectively.

$$pHpzc = \frac{(pK_a + pKb)}{2} \tag{7}$$

$$pK_a = -\log_{10}(K_a) \tag{8}$$

$$pK_b = -\log_{10}(K_b) \tag{9}$$

 $K_a$  and  $K_b$  represent acid and base disassociation constants of the oxide surface and their values are given in Table 1. The constant  $\beta$  is defined in Equation (10):

$$\beta = q^2 N_s \frac{\eta}{C_{eq} kT} \tag{10}$$

where  $N_s$  is the amount of site binding charges per unit area (values shown in Table 1), and  $C_{eq}$  and  $\eta$  are mentioned in Equation (11):

$$C_{eq} = \frac{C_{st} \times C_{dl}}{C_{st} + C_{dl}}; \eta = 2\sqrt{\frac{K_b}{K_a}}$$
(11)

where  $C_{dl}$  represents double-layer capacitance that is known as the Gouy–Chapman layer given by Equation (12) and  $C_{st}$  is known as a stern capacitance with a value of 0.2 F/m<sup>2</sup>:

$$C_{dl} = \sqrt{\frac{2Z_K^2 \varepsilon_w q n_0}{V_{th}}} \tag{12}$$

where  $\varepsilon_w$  represents the dielectric constant of water (80),  $Z_k$  is the valency of the  $K_{th}$  ion, as the solution contains only NaCl and both ions Na<sup>+</sup> and Cl<sup>-</sup> have a valency of one, so it is considered to be one and  $n_0$  is an ion concentration of electrolyte which is the same as intrinsic carrier density, so it can be expressed as Equation (13):

$$n_0 = n_i = q_{eff} \times N_{avo} \tag{13}$$

where  $q_{eff}$  represents effective ionic charge and  $N_{avo}$  is Avogadro's number which is equal to  $6.023 \times 10^{23}$ /mol.

Symbol	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	HfO <sub>2</sub>	Ta <sub>2</sub> O <sub>5</sub>	Ref.
ε <sub>rel</sub>	14	3.9	25	22	[43]
$Ns ({\rm cm}^{-2})$	8  imes 1014	5  imes 1014	4  imes 1014	10  imes 1014	[43]
рК <sub>а</sub>	6	-2	7	2	[43]
$pK_b$	10	6	7	4	[43]
Bandgap (eV)	8.8	9	5.7	5.3	[44]

Table 1. Values of parameters of different gate oxide materials.

For ISFETs, the interface charge density variation that occurs at the semiconductor channel and oxide interface depends on the variation in potential stirring at the oxide/fluid interface and is given by Equation (14):

$$\Delta\sigma_{sc} = -C_{ox}\Delta\psi_0 = -\frac{\varepsilon_0\varepsilon_{ox}}{t}\Delta\psi_0 \tag{14}$$

where  $\Delta \sigma_{sc}$  is the interface charge density,  $C_{ox}$  is oxide capacitance,  $\Delta \psi_0$  is the change in surface potential at the oxide/electrolyte interface, t is the thickness of the oxide layer,

and  $\varepsilon_{ox}$  is the relative permittivity of the oxide layer. In order to calculate the change in surface potential ( $\Delta \psi_0$ ) that occurs at the surface, Equation (6) can be used, and at a corresponding pH the value of the interface charge density is obtained with Equation (14), and these values of interface charge density at the channel/oxide interface can be used as a parameter for modeling of pH values. Assuming the solution to be 0.001 × PBS surface charge density is calculated.

#### 3. Results

The performance of our proposed pentacene-based DG-OFET was measured to understand the basic operations and characteristics of the device. It is observed from the simulated device characteristics that our device shows typical *p*-type transistor behaviour and is typically shown in both drain and transfer characteristics. Calibration in simulation parameters has been done in order to match the characteristics (as shown in Figure 2) by replicating the results obtained experimentally in the Ref. [25].



**Figure 2.** Calibration of a simulation result of drain current ( $I_{ds}$ )-gate voltage ( $V_{gs}$ ) characteristics with published experimental data Klauk. 2007 [25] for OFET.

In order to get the best possible match with the experimental results, the parameters of pentacene used include relative permittivity = 4.0, electron mobility  $(\mu_n) = 5 \times 10^{-5} \text{ cm}^2/\text{Vs}$ , hole mobility  $(\mu_p) = 0.85 \text{ cm}^2/\text{Vs}$ , conduction band density of states at 300 K =  $10^{21} \text{ cm}^{-3}$ , valence band density of states at 300 K =  $10^{21} \text{ cm}^{-3}$ , bandgap (eg300) = 2.2 eV. Figure 3a shows the drain characteristics of DG-OFET measured at gate voltages  $V_{gs} = -5 \text{ V}$ , -10 V, -15 V, and -20 V when  $V_{ds}$  is swept from 0 to -20 V with a step size of 1 V and transfer characteristics of a DG-OFET 3(b)log scale (inset in linear scale) are simulated at drain voltages  $V_{ds} = -5 \text{ V}$ , -10 V, -15 V, and -20 V when  $V_{gs}$  is swept from 0 to -20 V with a step size of 1.0 V.

Channel material was kept pentacene for these simulations, whereas the oxide was changed with SiO<sub>2</sub>, HfO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub>, respectively. Figure 4 shows the variation of the drain current ( $I_{ds}$ ) vs. gate voltage ( $V_g$ ) (transfer characteristics) curve for pH varying from 1 to 10 for DG-OFET with SiO<sub>2</sub> as a dielectric. Modelling of the pH value was performed in the form of interface charge density. The shift in drain current was towards the right as the value of the pH increased. The choice of oxide may help in many ways from high sensitivity to a longer device carrier lifetime. The electrolyte can be acidic or basic so its contact might imitate the device working and may damage the oxide, which in turn will affect the site binding charge and consequently affect the performance of the device. The choice of oxide may also influence power consumption. The choice must be based on whether we want more sensitivity or more energy to be saved. SiO<sub>2</sub> has long been used as an oxide for its easy availability, and hence, change is experienced in the form of a threshold voltage. The



simulation has been performed at  $V_{ds} = -3 V$  and  $V_{gs} = -8 V$  and results have been plotted in the logarithmic *y*-axis.

**Figure 3.** (a) The drain characteristics of DG-OFET at gate voltages  $V_{gs} = -5 V$ , -10 V, -15 V, and -20 V when  $V_{ds}$  is swept from 0 to -20 V with a step size of 1 V. (b) The transfer characteristics of DG-OFET log scale (Inset is linear scale) are at drain voltages  $V_{ds} = -5 V$ , -10 V, -15 V, and -20 V when  $V_{gs}$  is swept from 0 to -20 V with a step size of 1 V.



Figure 4. Drain current  $(I_{ds})$  vs. gate voltage  $(V_{gs})$  as a function of pH varying from 1 to 10.

The variation of the energy band for the same DG-OFET is shown in Figure 5a,b. A cutline was made at 1 nm below the oxide–channel interface at Vgs = 0 V, Vds = 0 V and Vgs = -8 V, Vds = -3 V and the energy levels of HOMO and LUMO were extracted. The source and the drain were connected by a semiconductor and the gate was separated from the channel by a layer of insulator. Under the no-bias condition, that is, when no (potential difference) was applied on the gate, due to the energy difference between the metal Fermi level and the semiconductor Fermi level, band-bending was induced. Thus, a large concentration of holes formed on the interface of the semiconductor and the insulator. When a sufficient bias was applied on the gate contact, the bent band became flat. Figure 5c shows the variation of HOMO and LUMO for pH values of 1, 5 and 10 for DG-OFET, respectively. When pH was changed by causing a change in surface potential, thereby causing an increase in current density, it resulted in band-bending. From the graph, it is clear that with an increase in pH, band-bending increases.



**Figure 5.** (**a**,**b**) Band-bending in the valance band and conduction band under no bias and bias conditions for pH = 1 and pH = 10; (**c**) variation of energy band for three values of pH = 1, 5 and 10 for the DG-OFET-based pH sensor, respectively.

Figure 6a,b shows the plot of electric field distribution and potential along the length of the channel of the proposed device. The plot was drawn by taking a cutline at 1 nm below the oxide semiconductor interface at  $V_{GS} = -8$  V and  $V_{DS} = -3$  V, respectively. With the change in pH from 1 to 10, it can be observed that the potential decreases, whereas the electric field increases. A high electric field is achieved at pH = 10, whereas the potential is at its lowest at pH = 1.



**Figure 6.** (a) The electric field along the device length. (b) The potential along the device length for pH = 1, 5 and 10 at  $V_{CS} = -8$  V and  $V_{DS} = -3$  V, respectively.

In order to estimate the sensing ability of a biosensor or ISFET the utmost significant factors are voltage sensitivity  $(S_V)$  and current sensitivity  $(S_I)$ . Traditionally, in FET-based biosensors, the sensitivity is used for the evaluation of the performance of the device and is calculated as a shift in threshold voltage or ratio of change of drain current at a particular gate voltage. We calculated current and voltage sensitivities as per work done by Liu et al. [45]. Voltage sensitivity ( $S_V$ ) is calculated for a constant value of the drain current  $(I_{REF})$ . For a definite value of the drain current  $(I_{REF})$ , the corresponding responsive gate voltage (V<sub>R</sub>) was obtained and the shift in that gate voltage ( $\Delta V_R$ ) with respect to a pH value could be used to find voltage sensitivity (S<sub>V</sub>). We calculated  $\Delta V_R$  for a specific value of I<sub>REF</sub> as  $\Delta V_R$  (at any pH) =  $V_R$  (at any pH) –  $V_R$  (at pH = 1). In our investigation, for the sake of simplicity, we did not incorporate interface traps in the simulation. However, in OFETs due to the presence of multiple layers of dissimilar electronic materials, such as metal electrodes, organic semiconductors, and dielectrics, following one another charge carrier, trapping within the device is caused by the existence of traps in both the metal/semiconductor interface and the dielectric/organic semiconductor interface. Figure 7 shows the curve of  $\Delta V_R$  vs. pH for reference values of drain current (I<sub>REF</sub>) = 10<sup>-5</sup> A, 10<sup>-6</sup> A, and 10<sup>-7</sup> A. The voltage sensitivity (Sv) attained by the DG-OFET device without taking traps (interface states) into consideration with SiO<sub>2</sub> as a dielectric for  $I_{REF}$  values of  $10^{-5}$  A,  $10^{-6}$  A, and  $10^{-7}$  A are 217.53 mV/pH, 142.99 mV/pH, and 146.26 mV/pH respectively. However, by considering traps, the voltage sensitivity (S<sub>V</sub>) attained by a DG-OFET device with SiO<sub>2</sub> as a dielectric for I<sub>REF</sub> values of  $10^{-5}$  A,  $10^{-6}$  A, and  $10^{-7}$  A are 227.99 mV/pH, 158.21 mV/pH, and 148.75 mV/pH. From the results obtained, it is quite clear that interface states do not affect the device sensitivity much.



**Figure 7.** Variation of responsive gate voltage ( $\Delta V_R$ ) with pH for drain current of (I<sub>REF</sub>) of 10<sup>-5</sup>, 10<sup>-6</sup>, and 10<sup>-7</sup> A/µm.

The drain current sensitivity (S<sub>DRAIN</sub>) represents the ratio of change of drain current as a function of V<sub>GS</sub>. The distinction in the drain current can be used as an electrical factor to sense the change in pH. Thus, the drain current sensitivity is defined as S<sub>drain</sub> [46] and is calculated as S<sub>drain</sub> = [I<sub>drain</sub> (at any pH) - I<sub>0</sub>/I<sub>0</sub>] where I<sub>0</sub> is the drain current obtained at pH = 1. Figure 8 shows the current sensitivity of DG-OFET devices with SiO<sub>2</sub> as a dielectric, and it can be seen that the maximum sensitivity achieved by the devices is nearly greater than 10<sup>6</sup> for pH = 10, while taking current at pH = 1 as a reference (I<sub>0</sub>).



Figure 8. Drain current sensitivity as a function of  $V_{GS}$  at different pH values ranging from 1 to 10.

As we already achieved sensitivity way beyond the Nernst limit, we further discuss how the sensitivity, device performance and stability can further be increased in the DG-OFET device. From Equation (14) it is concluded that by reducing the oxide thickness, the change in the interface charge density can be improved, but reducing the thickness of conventionally used SiO<sub>2</sub> leads to an increase in leakage current, thereby impairing the device characteristics. This leakage increases more when the device is operated in ionic fluids. In order to increase the sensitivity, another method is to use high-k dielectric material as oxide. Using high-k dielectric material can reduce leakage current by an increase in oxide thickness and thus enhances the stability of the device when used in ionic fluids [44]. The reactions that occur at the oxide/electrolyte interface for oxides like HfO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub> are similar to that of SiO<sub>2</sub> [29]. Thus, we replaced the oxide layer underneath the underlapped region from SiO<sub>2</sub> to HfO<sub>2</sub> without changing the capacitance (C<sub>ox</sub>) of the oxide layer and the oxide capacitance is given as in (15):

$$C_{ox} = \frac{\varepsilon_0 \varepsilon_{ox}}{t} \tag{15}$$

The increase in dielectric constant of HfO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub> was compensated by increasing the oxide thickness. Originally, the thickness for SiO<sub>2</sub> was taken as 3 nm, which increased to nearly 19.2 nm and 16.9 nm for HfO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub> to yield the same oxide capacitance. Figure 9a shows the variation of transfer characteristics with respect to pH with HfO<sub>2</sub> as a dielectric. Now coming towards the sensitivities of the device, Figure 9b shows the variation of responsive gate voltage  $\Delta V_R$  with pH for the drain current (I<sub>REF</sub>) values of  $10^{-5}$ ,  $10^{-6}$  and  $10^{-7}$  A/µm. The voltage sensitivities obtained for the HfO<sub>2</sub>-based DG-OFET device are 333.88 mV/pH, 155.179 mV/pH and 102.601 mV/pH for I<sub>REF</sub> of  $10^{-5}$  A,  $10^{-6}$  A and  $10^{-7}$  A, respectively, as shown in Figure 9b. The drain current sensitivity for the same dielectric is shown in Figure 9c. This is similar to when Ta<sub>2</sub>O<sub>5</sub> is used as oxide.

Figure 10a shows the variation of transfer characteristics with respect to pH with  $Ta_2O_5$  as a dielectric. Figure 10b shows the variation of the responsive gate voltage  $\Delta V_R$  with pH for the drain current (Iref) values of  $10^{-5}$  A,  $10^{-6}$  A and  $10^{-7}$  A. The voltage sensitivities obtained for the  $Ta_2O_5$ -based DG-OFET device are 555.284 mV/pH, 445.989 mV/pH and 439.00 mV/pH. Current sensitivity also increases with a change in the oxide from HfO<sub>2</sub> to  $Ta_2O_5$ .



**Figure 9.** (a) Drain current ( $I_{ds}$ ) vs. gate voltage ( $V_g$ ) as a function of pH that varies from 1 to 10 (b) Variation of responsive gate voltage ( $\Delta V_R$ ) with pH for drain current of ( $I_{REF}$ ) of 10<sup>-5</sup> A, 10<sup>-6</sup> A, and 10<sup>-7</sup> A, respectively, and (c) drain current sensitivity as a function of  $V_{CS}$  at pH values 1 to 10.



**Figure 10.** (a) Drain current ( $I_{ds}$ ) vs. gate voltage ( $V_g$ ) as a function of pH that varies from 1 to 10. (b) Variation of responsive gate voltage ( $\Delta V_R$ ) with pH for drain current of ( $I_{REF}$ ) of  $10^{-5}$  A,  $10^{-6}$  A, and  $10^{-7}$  A, respectively. (c) Drain current sensitivity as a function of  $V_{GS}$  at different pH values ranging from 1 to 10.

Finally, the maximum voltage sensitivity achieved by the DG-OFET pH sensor using different oxides is compared and shown in Figure 11a. The use of  $Ta_2O_5$  as a dielectric increases the voltage sensitivity of the device, and hence, the highest voltage sensitivity is achieved by the use of  $Ta_2O_5$  as a dielectric. Figure 11b shows the comparison of voltage sensitivity achieved in our work to that of previous work done in the same field [14,43,47–49].





### 4. Conclusions

A pH recognition with high resolution has gained enormous research attention over the past decade, and such sensors are needed to detect malignant tumors and other diseases in human blood. In this work, a detailed study of a dual-gate organic field effect transistor (pentacene) device having a source-sided underlapped region which is sensitive to an aqueous electrolyte environment was performed, the results showing that the DG-OFET based device can be preferred for the use of pH-sensing applications. The proposed device had a sensitivity of 217.53 mV/pH with SiO<sub>2</sub> as a gate oxide. Moreover, uses of the high-k dielectric can significantly increase the device sensitivity and help in less degradation over time. The maximum sensitivity achieved in our work using Ta<sub>2</sub>O<sub>5</sub> as a dielectric is 555.284 mV/pH, which is more than nine times the Nernstian limit.

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## References

- Dutta, J.C. Ion sensitive field effect transistor for applications in bioelectronic sensors: A research review. In Proceedings of the 2012 2nd National Conference on Computational Intelligence and Signal Processing (CISP), Guwahati, India, 2–3 March 2012; IEEE: New York, NY, USA, 2012; pp. 185–191.
- Manjakkal, L.; Szwagierczak, D.; Dahiya, R. Metal oxides based electrochemical pH sensors: Current progress and future perspectives. *Prog. Mater. Sci.* 2020, 109, 100635. [CrossRef]
- Wang, Y.; Yang, M.; Wu, C. Design and Implementation of a pH Sensor for Micro Solution Based on Nanostructured Ion-Sensitive Field-Effect Transistor. Sensors 2020, 20, 6921. [CrossRef] [PubMed]
- Shirakawa, H.; Louis, E.J.; MacDiarmid, A.G.; Chiang, C.K.; Heeger, A.J. Synthesis of electrically conducting organic polymers: Halogen derivatives of polyacetylene, (CH)x. J. Chem. Soc. Chem. Commun. 1977, 16, 578–580. [CrossRef]
- 5. Cui, T.; Liang, G. Dual-gate pentacene organic field-effect transistors based on a nano assembled SiO2 nanoparticle thin film as the gate dielectric layer. *Appl. Phys. Lett.* **2005**, *86*, 064102. [CrossRef]

- 6. Chen, F.C. Organic semiconductors. In Encyclopedia of Modern Optics; Elsevier: Amsterdam, The Netherlands, 2018; pp. 220–231.
- Jain, S.K.; Joshi, A.M. Dielectric-Modulated Double Gate Bilayer Electrode Organic Thin Film Transistor-based Biosensor for Label-Free Detection: Simulation Study and Sensitivity Analysis. *arXiv* 2022, arXiv:2205.15041.
- Rashid, S.; Bashir, F.; Khanday, F.A. Dielectrically Modulated Label Free Metal Controlled Organic Thin Film Transistor for Biosensing Applications. *IEEE Sens. J.* 2021, 21, 18318–18325. [CrossRef]
- Arias, A.C.; MacKenzie, J.D.; McCulloch, I.; Rivnay, J.; Salleo, A. Materials and Applications for Large Area Electronics: Solution-Based Approaches. *Chem. Rev.* 2010, 110, 3–24. [CrossRef]
- 10. Kang, B.; Lee, W.H.; Cho, K. Recent Advances in Organic Transistor Printing Processes. *ACS Appl. Mater. Interfaces* **2013**, *5*, 2302–2315. [CrossRef]
- 11. Fukuda, K.; Someya, T. Recent Progress in the Development of Printed Thin-Film Transistors and Circuits with High-Resolution Printing Technology. *Adv. Mater.* 2016, 29, 1602736. [CrossRef]
- Gundlach, D.J.; Shur, M.S.; Jackson, T.; Kanicki, J.; Martin, S.; Dodabalapur, A.; Crone, B. Electrical Behavior of Organic Transistors and Circuits. In *Printed Organic and Molecular Electronics*; Springer: Boston, MA, USA, 2004; pp. 347–524.
- Gundlach, D.J.; Lin, Y.Y.; Jackson, T.N.; Nelson, S.F.; Schlom, D.G. Pentacene organic thin-film transistors-molecular ordering and mobility. *IEEE Electron Device Lett.* 1997, 18, 87–89. [CrossRef]
- 14. Bartic, C.; Palan, B.; Campitelli, A.; Borghs, G. Monitoring pH with organic-based field-effect transistors. *Sens. Actuators B Chem.* **2002**, *83*, 115–122. [CrossRef]
- Gao, C.; Zhu, X.; Choi, J.-W.; Ahn, C. A disposable polymer field effect transistor (FET) for pH measurement. In Proceedings of the TRANSDUCERS 03, 12th International Conference on Solid-State Sensors, Actuators and Microsystems, Boston, MA, USA, 8–12 June 2003; Digest of Technical Papers (Cat. No. 03TH8664). IEEE: New York, NY, USA, 2003; Volume 2, pp. 1172–1175.
- 16. Torsi, L. Novel applications of organic based thin film transistors. *Microelectron. Reliab.* 2000, 40, 779–782. [CrossRef]
- 17. Torsi, L.; Dodabalapur, A.; Sabbatini, L.; Zambonin, P. Multi-parameter gas sensors based on organic thin-film-transistors. *Sens. Actuators B Chem.* **2000**, *67*, 312–316. [CrossRef]
- Torsi, L.; Cioffi, N.; Di Franco, C.; Sabbatini, L.; Zambonin, P.; Bleve-Zacheo, T. Organic thin film transistors: From active materials to novel applications. *Solid-State Electron.* 2001, *45*, 1479–1485. [CrossRef]
- 19. Caboni, A.; Orgiu, E.; Barbaro, M.; Bonfiglio, A. Flexible Organic Thin-Film Transistors for pH Monitoring. *IEEE Sens. J.* 2009, 9, 1963–1970. [CrossRef]
- Diallo, K.; Lemiti, M.; Tardy, J.; Bessueille, F.; Jaffrezic-Renault, N. Flexible pentacene ion sensitive field effect transistor with a hydrogenated silicon nitride surface treated Parylene top gate insulator. *Appl. Phys. Lett.* 2008, 93, 183305. [CrossRef]
- Spijkman, M.-J.; Brondijk, J.J.; Geuns, T.C.T.; Smits, E.C.P.; Cramer, T.; Zerbetto, F.; Stoliar, P.; Biscarini, F.; Blom, P.W.M.; de Leeuw, D.M. Dual-Gate Organic Field-Effect Transistors as Potentiometric Sensors in Aqueous Solution. *Adv. Funct. Mater.* 2010, 20, 898–905. [CrossRef]
- 22. Nguyen, T.; Seol, Y.; Lee, N.-E. Organic field-effect transistor with extended indium tin oxide gate structure for selective pH sensing. *Org. Electron.* 2011, *12*, 1815–1821. [CrossRef]
- Zhu, X.; Chong, H.A. pH sensor using nano electrodes in organic semiconductor. In Proceedings of the 26th Annual International Conference of the IEEE Engineering in Medicine and Biology Society, San Francisco, CA, USA, 1–5 September 2004; IEEE: New York, NY, USA, 2004; Volume 1, pp. 1968–1971.
- 24. Silvaco Inc. Device Simulation Software, Version 5.2.14.R; Silvaco Inc.: Santa Clara, CA, USA, 2013.
- 25. Klauk, H.; Zschieschang, U.; Halik, M. Low-voltage organic thin-film transistors with large transconductance. *J. Appl. Phys.* 2007, 102, 074514. [CrossRef]
- Lee, K.-W.; Choi, S.-J.; Ahn, J.-H.; Moon, D.-I.; Park, T.J.; Lee, S.Y.; Choi, Y.-K. An underlap field-effect transistor for electrical detection of influenza. *Appl. Phys. Lett.* 2010, 96, 033703. [CrossRef]
- Kim, J.-Y.; Ahn, J.-H.; Choi, S.-J.; Im, M.; Kim, S.; Duarte, J.P.; Kim, C.-H.; Park, T.J.; Lee, S.Y.; Choi, Y.-K. An underlap channelembedded field-effect transistor for biosensor application in watery and dry environment. *IEEE Trans. Nanotechnol.* 2012, 11, 390–394. [CrossRef]
- Kymissis, I. Organic Field Effect Transistors: Theory, Fabrication and Characterization; Springer Science Business Media: New York, NY, USA, 2008.
- Bandiziol, A.; Palestri, P.; Pittino, F.; Esseni, D.; Selmi, L. A TCAD-Based Methodology to Model the Site-Binding Charge at ISFET/Electrolyte Interfaces. *IEEE Trans. Electron Devices* 2015, 62, 3379–3386. [CrossRef]
- 30. Choi, B.; Lee, J.; Yoon, J.; Ahn, J.H.; Park, T.J.; Kim, D.M.; Kim, D.M.; Choi, S.J. TCAD-based simulation method for the electrolyte–insulator–semiconductor field-effect transistor. *IEEE Trans. Electron Devices* **2015**, *62*, 1072–1075. [CrossRef]
- 31. Pittino, F.; Palestri, P.; Scarbolo, P.; Esseni, D.; Selmi, L. Models for the use of commercial TCAD in the analysis of silicon-based integrated biosensors. *Solid State Electron.* **2014**, *98*, 63–69. [CrossRef]
- 32. Dhar, R.; Kumar, N.; Garcia, C.P.; Georgiev, V. Assessing the Effect of Scaling High-Aspect-Ratio ISFET with Physical Model Interface for Nano-Biosensing Application. *Solid State Electron.* **2022**, *195*, 108374. [CrossRef]
- Koneshan, S.; Rasaiah, J.C.; Lynden-Bell, R.M.; Lee, S.H. Solvent structure, dynamics, and ion mobility in aqueous solutions at 25 C. J. Phys. Chem. B 1998, 102, 4193–4204. [CrossRef]
- Shim, C.H.; Maruoka, F.; Hattori, R. Structural analysis on organic thin-film transistor with device simulation. *IEEE Trans. Electron Devices* 2009, 57, 195–200. [CrossRef]

- 35. Kang, G.-W.; Park, K.-M.; Song, J.-H.; Lee, C.; Hwang, D. The electrical characteristics of pentacene-based organic field-effect transistors with polymer gate insulators. *Curr. Appl. Phys.* 2004, *5*, 297–301. [CrossRef]
- Minari, T.; Nemoto, T.; Isoda, S. Temperature and electric-field dependence of the mobility of a single-grain pentacene field-effect transistor. J. Appl. Phys. 2006, 99, 034506. [CrossRef]
- Wang, L.; Fine, D.; Basu, D.; Dodabalapur, A. Electric-field-dependent charge transport in organic thin-film transistors. J. Appl. Phys. 2007, 101, 054515. [CrossRef]
- 38. Dimitrakopoulos, C.D.; Malenfant, P.R. Organic thin film transistors for large area electronics. Adv. Mater. 2022, 14, 99–117. [CrossRef]
- 39. Estrada, M.; Cerdeira, A.; Puigdollers, J.; Reséndiz, L.; Pallares, J.; Marsal, L.F.; Voz, C.; Iñiguez, B. Accurate modeling and parameter extraction method for organic TFTs. *Solid State Electron*. **2005**, *49*, 1009–1016. [CrossRef]
- 40. Koster, L.J.A.; Mihailetchi, V.D.; Blom, P.W.M. Bimolecular recombination in polymer/fullerene bulk heterojunction solar cells. *Appl. Phys. Lett.* **2006**, *88*, 052104. [CrossRef]
- 41. Yates, D.E.; Levine, S.; Healy, T.W. Site-binding model of the electrical double layer at the oxide/water interface. *J. Chem. Soc. Faraday Trans. 1: Phys. Chem. Condens. Phases* **1974**, *70*, 1807–1818. [CrossRef]
- 42. Landheer, D.; Aers, G.; McKinnon, W.R.; Deen, M.J.; Ranuarez, J.C. Model for the field effect from layers of biological macromolecules on the gates of metal-oxide-semiconductor transistors. *J. Appl. Phys.* **2005**, *98*, 044701. [CrossRef]
- 43. Narang, R.; Saxena, M.; Gupta, M. Analytical Model of pH sensing Characteristics of Junctionless Silicon on Insulator ISFET. *IEEE Trans. Electron Devices* **2017**, *64*, 1742–1750. [CrossRef]
- Reddy, B.; Dorvel, B.R.; Go, J.; Nair, P.R.; Elibol, O.H.; Credo, G.M.; Daniels, J.S.; Chow, E.K.C.; Su, X.; Varma, M.; et al. High-k dielectric Al<sub>2</sub>O<sub>3</sub> nanowire and nanoplate field effect sensors for improved pH sensing. *Biomed. Microdevices* 2011, 13, 335–344. [CrossRef] [PubMed]
- 45. Liu, N.; Liu, Y.H.; Feng, P.; Zhu, L.Q.; Shi, Y.; Wan, Q. Enhancing the pH sensitivity by laterally synergic modulation in dual-gate electric-double-layer transistors. *Appl. Phys. Lett.* **2015**, *106*, 073507. [CrossRef]
- 46. Hafiz, S.A.; Iltesha; Ehteshamuddin, M.; Loan, S.A. Dielectrically Modulated Source-Engineered Charge-Plasma-Based Schottky-FET as a Label-Free Biosensor. *IEEE Trans. Electron Devices* **2019**, *66*, 1905–1910. [CrossRef]
- Pfattner, R.; Foudeh, A.M.; Chen, S.; Niu, W.; Matthews, J.R.; He, M.; Bao, Z. Dual-Gate Organic Field-Effect Transistor for pH Sensors with Tunable Sensitivity. *Adv. Electron. Mater.* 2018, *5*, 1800381. [CrossRef]
- Kumar, N.; Kumar, J.; Panda, S. Back-channel electrolyte-gated a-IGZO dual-gate thin-film transistor for enhancement of pH sensitivity over nernst limit. *IEEE Electron Device Lett.* 2016, 37, 500–503. [CrossRef]
- Dwivedi, P.; Singh, R.; Chauhan, Y.S. Crossing the Nernst Limit (59 mV/pH) of Sensitivity Through Tunneling Transistor-Based Biosensor. *IEEE Sens. J.* 2020, 21, 3233–3240. [CrossRef]

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