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J.D. Akrofi, M. Ebert, J.D. Reynolds, K. Sun, R. Hu, M.R.R. de Planque, H.M.H. Chong

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Multi-stack insulator to minimise threshold voltage drift in ZnO FET sensors operating in ionic solutions

J.D. Akrofi, M. Ebert, J.D. Reynolds, K. Sun, R. Hu, M.R.R. de Planque, H.M.H. Chong
jda1u17@soton.ac.uk
Faculty of Engineering and Physical Sciences
University of Southampton

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Abstract

FET biosensors operating in an electrolyte experience a monotonic, temporal and relatively slow change in threshold voltage caused by the hydration of the insulator layer between the electrolyte and the FET’s channel. Minimising this temporal change in threshold voltage is critical as, over time, the drain current of n-channel FETs decreases, making it difficult to distinguish between the signal generated in response to analyte-receptor binding events and the background noise generated by the electrolyte and the FET biosensor. While Rapid Thermal Annealing of the insulator layer is known to diminish threshold voltage drift and its negative effects, it is not compatible with a low temperature fabrication process of 200°C. Our low temperature approach to minimising threshold voltage drift involves depositing a triple layer insulator stack, consisting of a layer of HfO2 between two Al2O3 layers. Wetting ZnO NWFETs with PBS (10 mM phosphate, 150 mM KCl, pH7.4) for an hour, showed that ZnO NWFETs with a stack insulator layer experienced a much smaller threshold voltage and drain current drift (100 mV, 0.064 nA) than ZnO NWFETs with a single material insulator layer (≥ 4300 mV, 2.72 nA), Aluminium oxide in this case. Having established the resilience enhancing properties of the stack insulator layer on FETs operating in electrolytes of physiological relevant ionic concentrations; ZnO NWFETs with a stack insulator layer were shown to be capable of detecting the presence of the miDNA-21 strands. This, in effect, paves the way for miRNA sensing experiments in the near future and for exploring the potential of ZnO NWFETs as a diagnostic tool.

Keywords: Field Effect Transistor biosensors; Zinc Oxide Nanowire Field Effect transistor; stack insulator layer; Threshold voltage drift; Phosphate Buffer Solutions; microDNA
1 Introduction

The duration of binding events between analyte and receptors at the surface of a FET biosensor (bioFET) can last anywhere from a few seconds to thousands of seconds. The length of time depends on a number of factors including the ionic strength of the surrounding solution; the concentration of analyte in solution; the binding affinity of the analyte to the receptors at the surface; and the mechanism by which the analyte is delivered to the surface of the bioFET [1]. It is, therefore, imperative that bioFETs can operate stably in solution for long periods of time (i.e. ≥ 1000 seconds) in order to register the response associated with analyte-receptor binding events.

When bioFETs come into contact with an aqueous solution during the course of a biosensing experiment, they experience a monotonic, temporal and relatively slow change in threshold voltage commonly referred to as drift. This change in threshold voltage is not caused by the analyte or by variations in the electrolyte composition but, in large part, by the hydration of the gate insulator layer between the electrolyte and the bioFET’s channel [2]. During hydration, bonds are formed between OH groups in water and the metal/metalloid atoms in the gate insulator [3] such as SiO$_2$, Si$_3$N$_4$, Al$_2$O$_3$ and Ta$_2$O$_5$, with the reaction being facilitated by the presence of traps and buried surface sites in the insulator. Jamasb et al [4] modelled the growth of a thin, hydrated layer at the surface of the insulator limited by the dispersive transport of water molecules; and showed, theoretically and by experimentation, that the temporal growth of this hydrated layer reduces the effective capacitance of the gate insulator. This reduction occurs because the hydrated section of the insulator layer has a smaller dielectric constant than the underlying, unmodified, insulator layer which also decreases in thickness as, over time, the hydrated layer grows. Consequently, the effective capacitance of the insulator, calculated as the capacitance of the hydrated layer in series with the thinner underlying, unmodified, insulator layer decreases as the hydrated layer grows.

Typically, for n-channel bioFETs a decreasing insulator capacitance would lead to a positive voltage drift. That is to say, over time, the threshold voltage would increase leading to a decrease in the output drain current. Not only does a decreasing output drain current, resulting from threshold voltage drift, dampen any change in current associated with analyte-receptor binding events; it makes it difficult to distinguish between the signal generated by the binding event and the background noise generated by the electrolyte and the bioFET itself. Due to the
variance in the duration of binding events (i.e. a few seconds to thousands of seconds) between analyte and receptors, it is of critical importance that the magnitude of threshold voltage drift is kept to a minimum so as to minimise the negative effects of a diminishing drain current on the function of bioFETs.

Mitigating the effects of threshold voltage drift by the Rapid Thermal Annealing (RTA) of the insulator layer, which reduces the density of hydration facilitating defects such as buried surface sites and traps, has been shown to be quite effective [5] [6]. However, RTA is not a viable option when employing a low temperature fabrication process of 200°C [7]. This paper presents a low temperature approach to mitigating threshold voltage drift which is centered around depositing a multi-material stack of high-$\kappa$ dielectric insulators via Plasma Enhanced Atomic Layer Deposition (PEALD). As opposed to the current bioFET design and fabrication standard, which is to deposit a single material high-$\kappa$ dielectric insulator layer, a stack of appropriately chosen high-$\kappa$ dielectric insulators will have a larger effective capacitance making it a more potent transducer [8]. More importantly, the effects of hydration are less pronounced on the stack than the single material insulator layer. This is because the change in the effective capacitance, resulting from the presence of the hydrated layer, is smaller for the stack than for the single material insulator layer where, the effective capacitance is calculated as the capacitance of the hydrated layer in series with the underlying, unmodified, insulator layers. As a result, the bioFET with a stack insulator will experience a smaller threshold voltage drift and drain current shift than the bioFET with a single material insulator layer.

2 Fabrication and Experimentation

To demonstrate this phenomenon, a novel dry etch lift off technique [9] was used to fabricate two devices comprised of 512 Zinc Oxide (ZnO) Nanowire Field effect transistor (NWFETs) arrays (Figure 1(a)) at 150°C. ZnO in its wurtzite form is naturally a n-type semiconductor [10] and it has a large and direct band-gap (3.37 eV [11]) making it an attractive material for electronic applications. Its large band-gap gives this material the ability to sustain large electric fields and withstand higher breakdown voltages, while enabling lower noise generation, and high temperature and power operation [12]. Using PEALD, a stack insulator layer consisting of 4 nm of HfO$_2$ between two 8 nm Al$_2$O$_3$ layers was deposited on one device Figure 1(c); 24 nm of Al$_2$O$_3$
was deposited on the other device (d) to be used as a control device. For all Al₂O₃ depositions the substrate was heated to 150°C and 200°C for HfO₂ deposition. Although HfO₂ has a much larger dielectric constant than Al₂O₃ [13] it does suffer from non-ideal effects namely, hysteresis phenomenon [14]. Al₂O₃ has been shown to have a stronger resistance to these non-ideal effects [15] than HfO₂ and is also known to be more compatible with 3-Aminopropyltriethoxysilane (APTES), a commonly used cross linker molecule, thus a greater number of biomolecules can be immobilised at the surface of an Al₂O₃ insulator than a HfO₂ insulator [16]. It is for these reasons that Al₂O₃ was used as the single material insulator layer and the sandwich configuration was adopted for the stack insulator layer, in order to minimise the amount of HfO₂ used.

Figure 1: (a) An optical image of a chip consisting of 512 ZnO NW FET arrays with gate lengths of 20 μm, 30 μm, 40 μm, 60 μm and 90 μm. An NW FET array with a 20 μm gate was used in each of the experiments reported in this paper. (b) Top view scanning electron micrograph of the NW FETs. (c) Schematic of the cross section of the NW FET with a stack insulator layer. (d) Schematic of the cross section of the NW FET with an Al₂O₃ insulator layer.

Figure 2: (a) An image of ZnO NW FETs underneath a sheet of PMMA laser cut to form channels through which to flow PBS from a syringe to wet the surface of the NW FETs. The width of the channels is 1.18 mm. (b) The protocol for the experiment investigating the threshold voltage drift mitigating effects of the stack insulator layer. Both the ZnO NW FETs with the stack insulator layer and the ZnO NW FETs with the Al₂O₃ insulator layer underwent this protocol. (c) The experimental protocol for the proof of concept miDNA sensing investigation.

To investigate whether ZnO NW FETs with a stack insulator layer have a lower hydration related threshold voltage drift than ZnO NW FETs with a single material (Al₂O₃) insulator layer; Phosphate Buffered Solution (PBS) (10 mM phosphate, 150 mM KCl, pH 7.4) was delivered to the surface of each device through laser cut poly methyl methacrylate (PMMA) microfluidic channels Figure 2(a). The ionic strength of the PBS used in this experiment was made up to 150 mM (Debye length of 0.7 nm) because the ionic strength of most physiological samples is ≥ 100 mM [17], [18], [19]. IᵥD VᵥG sweeps were recorded before and after both devices were wetted with PBS, in dry conditions. In the subsequent hour, while each device was wetted with PBS, the drain current was
recorded. For this current-time wet measurement, both devices were biased in the subthreshold region with a gate voltage of 4 V and a drain voltage of 2 V. The devices were biased in the subthreshold region as it has been shown to be the most sensitive region of bioFET operation for concentration related sensing [20]. That is to say, bioFETs are most sensitive to changes in analyte concentration when operating in this region; and as these are the kinds of future sensing experiments we aim to be conducting, biasing in the subthreshold region was deemed to be expedient. Moreover it enables the NWFETs to be employed as low power devices.

Following the investigation into the drift minimising effects of the stack insulator layer, a proof of concept experiment was implemented to demonstrate the potential of ZnO NWFETs with a stack insulator layer as a biosensing tool. microDNA (miDNA) are the stable biological equivalent of microRNA (miRNA). miRNA are an important group of non-protein coding RNA molecules which regulate gene expression at the transcriptional and post-transcriptional level in wide range of animals, plants, and viruses [21]. The downregulation of miRNA is observed in a wide variety of cancers. As such, miRNA profiles can be used to deduce the developmental lineage and differentiation states of tumours [22], making miRNA a vital group of cancer diagnostic biomarkers. As miRNA are unstable molecules (i.e. degrade easily), equivalent microDNA (miDNA) strands are used in most proof of concept experiments to demonstrate the ability of a device to detect miRNA [23]. The analyte used in this experiment was 100 nM of miDNA-21 in Trisma-EDTA (TE) Buffer (20 μM Trizma, 100 μM KCl, 2 μM EDTA). This buffer solution had a Debye length of, approximately, 30 nm. The protocol pictured in Figure 2(c) describes how the experiment was conducted.

A fresh device also consisting of 512 ZnO NWFET array with a stack insulator layer was used for this experiment. This device was also biased in the subthreshold region however, in this instance, with a gate voltage of 1.2 V and a drain voltage of 3 V. Although this device was identical to the ones used in the previous experiments, its characteristic were slightly different hence the different bias voltages. All electrical measurements were conducted in a dark environment, at room temperature, using the Keysight Semiconductor Parameter Analyzer (B1500A). It is important to note that all drain current - time measurements involving buffer solution without miDNA-21 are control measurements and that the reason for allowing the buffer solution to evaporate was to ensure that the strands of miDNA-21 physisored to the surface of the stack insulator layer. This was done in the absence of a functionalisation step which would have,
unnecessarily, prolonged this proof of concept experiment.

3 Results & Discussion

Figure 3(a) shows $I_D V_G$ curves for both devices in dry conditions. As mentioned above, the bias voltages chosen for both devices were a gate voltage of 4 V and a drain voltage of 2 V. The data generated from the $I_D V_G$ sweeps in Figure 3(a) showed that these bias voltages produced a 1.40 nA current for the ZnO NWFETs with the stack insulator and 2.79 nA current for ZnO NWFETs with the Al$_2$O$_3$ insulator. Figure 3(b) depicts how the drain current of each device varies over an hour when wetted with PBS. In comparing the drain current before and after PBS was initially delivered to the surfaces of both devices, it was seen that the drain current of the ZnO NWFETs with the Al$_2$O$_3$ insulator had shifted by 2.72 nA to a value of 73.8 pA (left axis of Figure 3(b)) by the end of the experiment. Although the drain current of this device exhibited some stability over the course of the experiment (i.e. drain current variability, roughly, 2 pA during the experiment), the magnitude of the drain current of this device was in the range of the leakage current. Hydration causing a bioFET to drift into the range of leakage current is detrimental to its function as biosensor, as negatively charged analyte such as DNA would have the effect on n-channel bioFETs of decreasing the drain current. Consequently, any change in current associated with an analyte-receptor binding event will be virtually indistinguishable from the leakage current, thus rendering such a bioFET effectively useless.

Figure 3: (a) $I_D V_G$ curves of the ZnO NWFETs before they were wetted with PBS (step 1 in Figure 2(b)). (INSET) $I_D V_G$ curves of the ZnO NWFETs after being wetted with PBS (step 5 in Figure 2(b)). (b) Drain Current against Time graph for NWFETs while wetted with PBS (step 3 in Figure 2(b)). Both devices were biased with in the subthreshold region (gate = 4 V; drain= 2 V) where each is producing nano Amp currents an order of magnitude above the leakage current. The time resolution is 60s for each curve, with both curves showing a slight increase in current as they stabilise over the course of the experiment.

Figure 4: (a) Drain Current against Time graph for ZnO NWFETs with a stack insulator in TE Buffer and then in a solution of TE Buffer with 100 nM miDNA-21 (steps 2 and 9 in Figure 2(c)).
(b) Drain Current against Time graph of the NWFETs in rehydrated TE Buffer and then in a rehydrated solution of TE Buffer with 100 nM miDNA-21 (steps 5 and 13 in Figure 2(c)). Both graphs (a) and (b) show fluctuations in the signal which might be due to miDNA strands detaching then reattaching to surface of the ZnO NWFETs. (c) Drain Current against Time graph for NWFETs obtained after TE Buffer was allowed to evaporate (steps 4 and 11 in Figure 2(c)).

As seen in the $I_DV_G$ sweep of the same device, taken after the wet measurement Figure 3(a) (inset), the drain and leakage currents of this device have both increased by two orders of magnitude. Furthermore, the drain current is yet to reach saturation even at a gate voltage of 10 V, indicating that the devices has not switched on by this point. That is to say, the threshold voltage the ZnO NWFETs with Al$_2$O$_3$ insulator layer is greater than 10 V. Given that the threshold voltage of this device, calculated using the $2^{nd}$ derivative method [24], was 5.7 V before it was wetted with PBS for an hour; we estimate the threshold voltage to have shifted by least 4300 mV over the duration of the wet measurement. To summarise, it is seen that the over course of an hour, the drain current and threshold voltage of the ZnO NWFETs with the Al$_2$O$_3$ insulator layer shifts by 2.72 nA and $\geq$ 4300 mV, respectively, when wetted with PBS.

The ZnO NWFETs with the stack insulator layer, in stark contrast, produced a significantly smaller change in drain current of 0.064 nA. This corresponded to a 100 mV threshold voltage drift over the course of the hour long investigation. During this period the drain current of this device showed quite remarkable stability as it only varied by 0.04 nA. Furthermore, the output current was 2 orders of magnitude above the leakage current range, thus eliminating any potential difficulties in differentiating between the leakage current and the output signal generated in response to an analyte-receptor binding event at the surface of NWFETs. The $I_DV_G$ sweep of the ZnO NWFETs with the stack layer taken after the wet measurement Figure 3(a) (inset), shows a devices which is still in working condition. Compared with the noisy $I_DV_G$ sweep of the barely functioning ZnO NWFETs with the Al$_2$O$_3$ layer, it emphasizes the enhanced protection against the detrimental effects of hydration that the stack insulator layer provides.

Table 1 summarises the results obtained which support the assertions made above. It was posited that while the insulator layers of both devices would be subject to hydration as a result of being wetted with an electrolyte; the reduction in effective capacitance of the stack insulator layer would be less than reduction in the capacitance of the single material Al$_2$O$_3$ insulator layer.
Consequently, the ZnO NWFETs with the stack layer would experience a smaller drift in threshold voltage and drain current than the ZnO NWFETs with the Al₂O₃ layer. The results in Table 1 also show that the ZnO NWFETs with the Al₂O₃ insulator layer experienced a threshold drift rate of 71.7 mV per minute which is of the same order of magnitude as measured bioFET responses [25], [26]. This large threshold voltage drift rate is indicative of a rapidly deteriorating device which, during a biosensing experiment, will drown the response generated by binding events between analyte and receptors. It is even conceivable that such a device might not even register a response especially in cases where the analyte concentration is low as binding events take much longer to occur in such instances. On the other hand, the ZnO NWFETs with the stack insulator layer was observed to have threshold voltage drift rate which was order of magnitude smaller than that observed for ZnO NWFETs with the Al₂O₃ layer. This indicates that the ZnO NWFETs with the stack layer would be able to produce a much more stable response over a longer period of time. The results obtained confirm that the stack layer enhances the resilience of ZnO NWFETs biosensors, operating in electrolytes of physiological relevant ionic concentrations, by minimising the drift in threshold voltage and drain current.

Table 1: A summary of the experimental results obtained.

<table>
<thead>
<tr>
<th>Devices</th>
<th>Magnitude of shift in drain current (nA)</th>
<th>Magnitude of threshold voltage drift (mV)</th>
<th>Threshold voltage drift rate (mV/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃/HfO₂/Al₂O₃ (Stack)</td>
<td>0 (nA)</td>
<td>100</td>
<td>1.67</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2.72</td>
<td>≥ 4300</td>
<td>71.7</td>
</tr>
</tbody>
</table>

The results obtained from the miDNA sensing experiment show a marked difference between the signal produced by the buffer solution and the signal produced by the miDNA in the buffer solution, in all drain current - time measurement phases of the investigation. The electric field of the negative charge on the miDNA strands, which physisorbed to the surface of the stack insulator, biases the ZnO NWFETs and causes its drain current to decrease as seen in Figure 4. There was at most a 27 nA and a 36 nA difference between the output signals shown in Figure 4(a) and Figure 4(b), respectively, over the course of the measurement. This difference was most pronounced when comparing output currents when the buffer solution is evaporated Figure 4(c).
There was at least a 78 nA difference between the signal produced by the evaporated buffer and signal produced by evaporated buffer with miDNA-21 over a 7200 second period, which was caused by the presence of miDNA strands. It should be noted that rehydration was a precautionary measure taken to identify if the evaporation of the buffer caused an aberration in the output signals (signals overlapping) or whether they followed the same trend as seen with the other measurements.

These results demonstrate the potential of the ZnO NWFTs with stack insulator as a bioFET. Moreover, the minimal threshold voltage drift and drain current shift seen in the previous investigation highlights the enhanced stability the stack insulator gives the ZnO NWFTs, and this will be extremely beneficial in future biosensing applications. While a number of bioFET sensing experiments report contrived output metrics such as percentage change in conductance and normalized responses [25] [27] [28], probably due to the lack of a strong, stable and distinguishable output drain current; the ZnO NWFTs with a stack insulator used in these experiments do not experience any of these issues and as such, one can easily follow how the raw output signal (drain current) varies during the experiment without needing to process the output signal. This will, in the long run, make it considerably easier for non-technical end users to use these bioFETs.

4 Conclusions

BioFETs operating in an electrolyte experience a monotonic, temporal, and relatively slow drift in threshold voltage caused by the hydration of the insulator layer between the electrolyte and the bioFET’s channel. It is imperative to the function of bioFETs that drift inducing effects of hydration are minimised as it results in a diminishing drain current. This makes it increasingly difficult to distinguish between the signal generated in response to analyte - receptor binding events and the background noise generated by the electrolyte and the bioFET itself. It has been shown that a tri-layer insulator stack of high-$\kappa$ dielectrics comprised of HfO$_2$ sandwiched between two Al$_2$O$_3$ layers experiences drift to lesser degree than a single material insulator layer comprised of Al$_2$O$_3$. This is because the stack insulator experiences a smaller, hydration related, change in effective capacitance than the single material insulator layer. Having established the resilience enhancing properties of the stack insulator on ZnO NWFTs operating in electrolytes of
physiological relevant ionic concentrations; ZnO NWFETs with a stack insulator were shown to be capable of detecting the presence of the miDNA-21 strands. These results pave the way for miRNA sensing experiments in the near future and for exploring the potential of the ZnO NWFETs as a diagnostic tool.

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Conflict of interest: None

References


Highlights

- FET biosensors operating in an electrolyte experience threshold voltage drift
- Voltage drift diminishes the response generated by analyte-receptor binding events
- Al$_2$O$_3$/HfO$_2$/Al$_2$O$_3$ stack deposited on ZnO nanowires was seen to reduce voltage drift
- Subsequently, ZnO nanowires with a stack were used to detect miDNA-21 strands
- This proof of concept experiment paves the way for future miRNA sensing experiments

Graphical abstract
Figure 2

(a) Image of a device with labeled Inlet and Outlet.

(b) Flowchart showing steps:
1. Wet surface of NWFETs with TE Buffer
2. Run Drain Current - Time measurement
3. Evaporate Buffer
4. Run Drain Current - Time measurement
5. Rehydrate the sensor's surface with DI water
6. Run Drain Current - Time measurement
7. Flush the sensor's surface with DI water and then air to remove buffer.
8. Deliver 100 nM of miDNA-21 in TE Buffer to the surface of the same set of NWFETs
9. Run Drain Current - Time measurement
10. Evaporate Buffer
11. Run Drain Current - Time measurement
12. Rehydrate the sensor's surface with DI water
13. Run Drain Current - Time measurement

(c) Detailed steps for each operation.
Figure 4

Drain Current against Time (Initial)
100 nM microDNA-21 in TE Buffer Solution
(10μM Trizma, 50μM KCl, 1μM EDTA, pH 8)

Drain Current against Time (Rehydrated)
100 nM microDNA-21 in TE Buffer Solution
(10μM Trizma, 50μM KCl, 1μM EDTA, pH 8)

Drain Current against Time (Buffer Evaporated)
100 nM microDNA-21 in TE Buffer Solution
(10μM Trizma, 50μM KCl, 1μM EDTA, pH 8)

TE Buffer Solution
(10μM Trizma, 50μM KCl, 1μM EDTA, pH 8)