

Comprehensive identification of sensitive and stable ISFET sensing layer high-k gate based on ISFET/electrolyte models

Ahmed M. Dinar¹, A.S. Mohd Zain², F. Salehuddin³

^{2,3}Faculty of Electronics and Computer Engineering, Universiti Teknikal Malaysia Melaka (UTeM), Malaysia

¹Computer Engineering, University of Technology, Baghdad, Iraq

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ABSTRACT

The ISFET sensing membrane is in direct contact with the electrolyte solution, determining the starting sensitivity of these devices. A SiO₂ gate dielectric shows a low response sensitivity and poor stability. This paper proposes a comprehensive identification of different high-k materials which can be used for this purpose, rather than SiO₂. The Gouy-Chapman and Gouy-Chapman-Stern models were combined with the Site-binding model, based on surface potential sensitivity, to achieve the work objectives. Five materials, namely Al₂O₃, Ta₂O₅, HfO₂, ZrO₂ and Sn₂O₃, which are commonly considered for micro-electronic applications, were compared. This study has identified that Ta₂O₅ have a high surface potential response at around 59mV/pH, and also exhibits high stability in different electrolyte concentrations. The models used have been validated with real experimental data, which achieved excellent agreement. The insights gained from this study may be of assistance to determine the suitability of different materials before progressing to expensive real ISFET fabrication.

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Corresponding Author:

Ahmed M. Dinar,

Faculty of Electronics and Computer Engineering,

Universiti Teknikal Malaysia Melaka (UTeM),

Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia.

Email: aezalzubdy@gmail.com

1. INTRODUCTION

There has been a tremendous convergence in the last decade in chemical sensing applications, with CMOS-based micro-technology playing a crucial role in this field. This has been enabled by the use of solid-state sensors that can be implemented in planar form, and manufactured using CMOS technology to monolithically integrated on a single chip. This technology now provides an opportunity for chemical sensing platforms to leverage semiconductor technology that may offer advantages such as scalability, miniaturisation, fabrication, and integration with intelligent instrumentation. ISFET sensors are the most promising, and may satisfy all these opportunities. The essential property of ISFETs is scalability with the developing semiconductor fabrication. This property provides a continuous trend of sensor minimisation, with resulting advantages for biochemical tests, e.g. fast response and the small volume of analyte solution required.

Due to its promising application in biological, biochemical and medical detection [1]-[5], ISFET has received much interest since it was first reported by Bergveld in 1972 [6]. Particularly, much effort has been made to investigate pH sensitive ISFETs with studies on device structures and pH-sensing membranes aimed at improving the sensitivity and stability of ISFETs [7], [8]. It is well known that the gate dielectric is in direct contact with the electrolyte solution, which determines the starting sensitivity of these devices. As the SiO₂ gate dielectric shows a low response sensitivity and poor stability, other inorganic materials such as Al₂O₃ [7], [8], Si₃N₄ [6], [9], Ta₂O₅ [11], [9], HfO₂ [12]-[15] and ZrO₂ [12]-[14] with their enhanced

stability and sensitivity have also been investigated. Moreover, the drain-source voltage of an ISFET based on a MOSFET structure also affects ionic charges with a horizontal electric field in the electrolyte solution, resulting in a non-uniform charge distribution at the electrolyte-insulator interface. The operating mechanism of a pH-sensitive ISFET is the change of potential between the electrolyte solution and the gate dielectric surface, thus leading to an increased or decreased output current by the ISFET. Moreover, using of Double Gate MOSFETs by prove the ISFET increase the subthreshold swing in case of different top and bottom gate oxide thicknesses [25], [26].

Until now, different models and adaptations of models have been used to model the pH-change sensitivity in ISFETs, the development of surface potential in the area, and in the further course of a Helmholtz double layer (DL). Louis Georges Gouy in 1910, and David Leonard Chapman in 1913, together noticed that capacitance was not a constant, but depended on the applied potential and the ionic concentration. The Gouy-Chapman model made an important contribution by proposing a diffuse model of the DL. In this model, “the charge distribution of ions as a function of distance from the metal surface allows Maxwell–Boltzmann statistics to be applied”. Thus, the electric potential decreases exponentially at distances further away from the surface of the fluid bulk. However, the Gouy-Chapman model fails for highly charged DLs. In 1924, Otto Stern suggested combining the Helmholtz model with the Gouy-Chapman model: In Stern's model, some ions adhere to the electrode as suggested by Helmholtz, giving an internal Stern layer, while some form a Gouy-Chapman diffuse layer. Figure 1 demonstrates schematic representations of electrical double layer structures describing (a) the Helmholtz model, (b) the Gouy–Chapman model and (c) the Gouy–Chapman–Stern model.

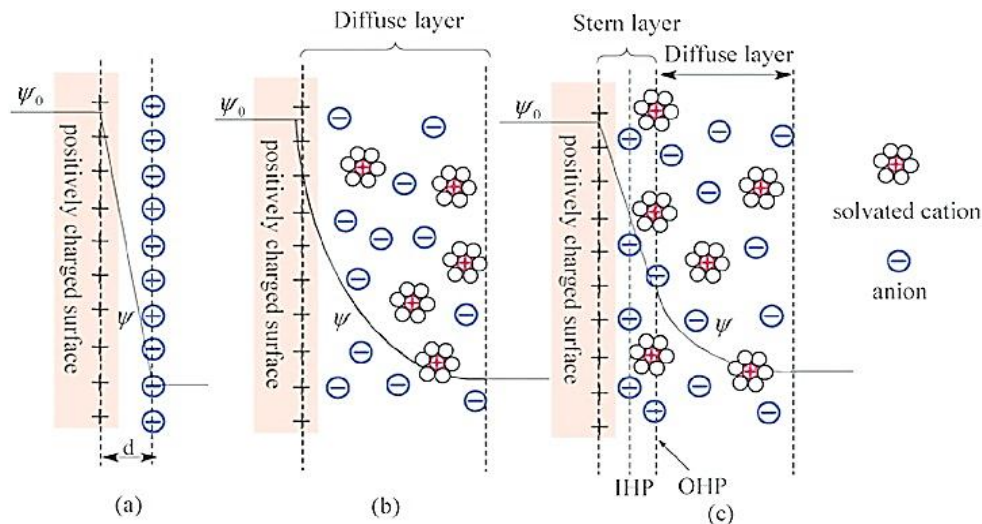


Figure 1. ISFET DL's models [16]

In this paper, we present a comprehensive identification of high pH-sensitivity insulator layer material (Stern Layer) based on a surface potential sensitivity parameter. The Gouy-Chapman and Gouy-Chapman-Stern models were combined with the Site-binding model to achieve the stated work objectives. The combination of these models will allow for a higher sensitivity using material that is more resistant to changes in electrolyte pH for ISFET insulator membranes, and furthermore, the identification of the specific capacitance of the Stern layer. Figure 2 below demonstrates the work objective in terms of insulator/electrolyte/semiconductor interfacing ISFETs.

The rest of the sections present the modelling and its validation with experimental real data as reported in Section 2. The model result and a discussion about the ISFET sensitivity of four high-k materials. Are reported in Section 3. Model limitations are mentioned in Section 4 and the conclusions are summarised in Section 5.

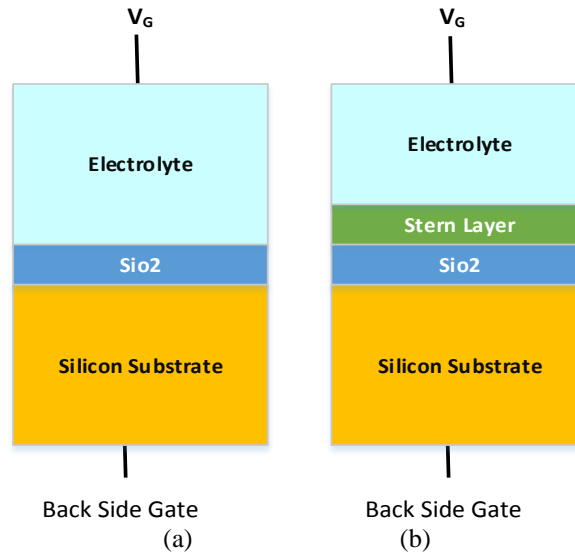


Figure 2. ISFET structure based on (a) Chapman model (b) Gouy-chapman-stern model

2. ISFET MODELS AND METHODS

2.1. ISFET modelling

The ISFET has been used for many years to measure the pH value of electrolyte solutions [17]-[21]. In the original structure of an ISFET, the gate oxide is in direct contact with the electrolyte solution as shown in Figure 2(a), acting as a sensing dielectric. The Stern layer is a modified version of the ISFET in which the sensing layer is separated from the gate oxide by using an extended conductive layer Figure 2b after the gate oxide is covered by the electrolyte solution, creating a more robust structure for extended efficacy in the solutions. The area of the sensing gate, compared to the area of the entire sensor, is one of the structural design parameters that greatly influence the electrical behaviour of the sensor, due to the existence of parasitic capacitance which degrades the measured sensitivity of the sensor. The build-up of a surface charge due to protonation/deprotonation reactions induces a potential at the sensor surface. Through the effective coupling capacitance between the sensor surface and Floating Gate (FG), the surface potential (ψ_0) modulates the potential of the FG, and therefore there will be a corresponding shift in the threshold voltage (V_T) of the sensor [22], [23]. Therefore, from the Site-binding model, the charge density can be expressed by [24]:

$$\sigma_0 = qN_{sil} \left(\frac{aH_s^{+2} - K_a K_b}{K_a K_b + K_b aH_s^+ + aH_s^{+2}} \right) \quad (1)$$

Where; aH_s^+ is the H^+ activity calculated by ($aH_s^+ = 10^{-pH_s}$); q is the elementary charge; N_{sil} is the density of the available sites and K_a ; K_b represents the intrinsic dissociation constants, and the N_{sil} , K_a and K_b , are oxide layer dependent.

Based on “charge density”, the charge on the electrolyte side of a double layer (σ_{DL}) is the same value, but is a negative charge. Therefore, this charge can be calculated from the integral double layer capacitance (C_i) and the surface potential [23]:

$$\sigma_{DL} = -C_i \psi_0 = -\sigma_0 \quad (2)$$

Therefore, by solving (1) and (2), we can demonstrate the relation between aH_s^+ and ψ_0 parameters.

According to the Boltzmann distribution model for the H^+ ions [8], [23], [24], the pH value at the sensor surface is [8]:

$$pH_s = pH_B + \frac{q \psi_0}{2.3kT} \quad (3)$$

T and k represent the absolute temperature and Boltzmann constant, respectively. The subscript S and B denote the pH at the sensor surface and in the bulk solution, respectively, and ψ_0 is the potential drop

across the diffusion layer. In Equation (3), the intrinsic buffer capacity (β_{int}) is defined as the ability to collect a charge at the sensor surface (σ_0) due to the change in surface pH (pHs)[8]:

$$\beta_{int} = \frac{\Delta\sigma_0}{-q \Delta pH_S} \quad (4)$$

The diffusion capacity (C_{diff}) is the ability to store the opposing charge in the solution near the surface, due to the change in surface potential [8]:

$$C_{diff} = \frac{\Delta\sigma_0}{\Delta\psi_0} \quad (5)$$

Therefore, we can write:

$$\frac{\Delta\psi_0}{\Delta pH_S} = -q \frac{\beta_{int}}{C_{diff}} \quad (6)$$

Differentiating Equation (3) with respect to the bulk pH, and using Equation (6), the surface potential sensitivity to the pH_B can be derived as [9].

$$\frac{\Delta\psi_0}{\Delta pH_B} = -2.3 \frac{kT}{q} \left(\frac{1}{1+\alpha} \right) \quad (7)$$

With,

$$\alpha = \frac{2.3 kT C_{diff}}{q^2 \beta_{int}} \quad (8)$$

Here, α is a positive sensitivity (dimensionless parameter). Therefore, the sensitivity of the potential at the sensor surface and the corresponding change of the sensor threshold voltage to the bulk pH are limited to 59.3 mV/pH (Nernst limit).

In the Stern model, the relationship between the diffusion layer potential ψ_0 (previous calculations) and the Stern potential ψ_s can be expressed by:

$$(\psi_0 - \psi_s) = \frac{(8kT\varepsilon\varepsilon_0 n^o)^{\frac{1}{2}} \sinh\left(\frac{zq\psi_s}{2kT}\right)}{C_S} \quad (9)$$

Where $\varepsilon\varepsilon_0$ is the permittivity of free space and its relative permittivity, respectively; n^o is the number concentration of each ion in the bulk, z is the magnitude of the charge on the ions and C_S represents the integral capacitance of the Stern layer.

2.2. Validation of the model

With the aim of checking the validity of our model, to show the significance of the Stern layer, and to demonstrate specific integral capacities, we extracted the sensitivity parameters and potential responses versus the pH_B curve for the structures reported in Figure 2, and adapted experimental real data for a comparison of results [9].

Figure 3(a) (Gouy-Chapman) shows the sensitivity parameters of SiO₂ as a function of pH_B at an 0.1 electrolyte concentration in the Gouy-Chapman model. As shown, the maximum surface potential sensitivity lies between pH 6.5 to pH 8. The lowest sensitivity up to zero charge is approximately (pH=2) due to a low β_{int} . As shown, perhaps the most serious disadvantage of this model is the curve roll-off when the pH becomes higher than pH=10. In contrast to earlier findings, however, no roll-off of the Stern model was detected, as shown in Figure 3(a). These findings will doubtless be much scrutinised, but there are some immediately dependable conclusions for total sensitivity as shown in Figure 3b. What can be clearly seen in this chart is the high rate of sensitivity achieved in the Stern model - closer to the Nernst level. Figure 4 is a comparison of the experimental real data with the theoretical response, using the two models for SiO₂. The sensitivity from experimental data is slightly higher than the theoretical sensitivity results. A Gouy-Chapman-Stern model with 0.2 C_s achieved a better fit with real data.

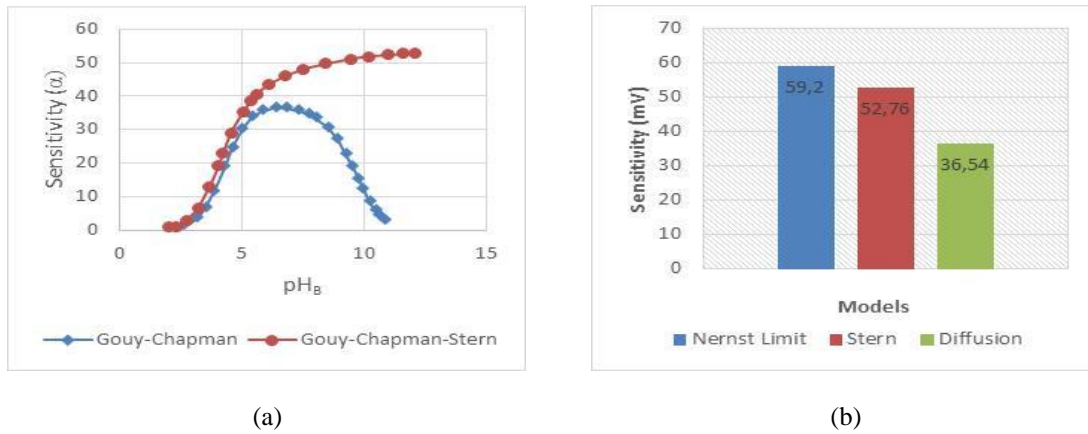


Figure 3. Theoretical and experimental sensitivities of ISFET: (a) SiO_2 sensitivity parameters for two models, and (b) Total sensitivity models comparing with Nernst limit

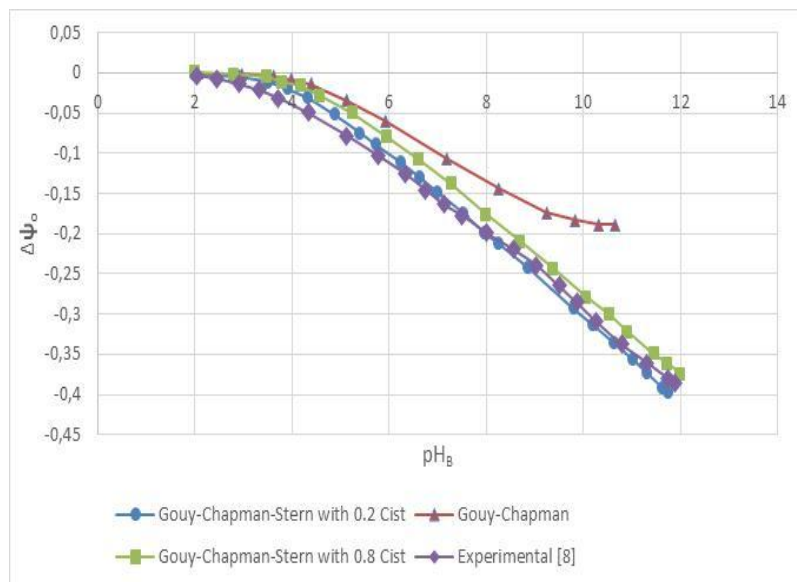


Figure 4. Theoretical and experimental total responses of a SiO_2

From the previous validation, we can conclude that the Stern layer with a specific end goal provide the significance to replicate the measurements at high pH. The reason is that when the cations collect at the base separation from the dielectric/electrolyte interface, a voltage drop is created over the Stern layer. Therefore, specifically in high pH bulk, instead of using a Stern layer, electrolyte ions will cover the surface charge causing threshold voltage weakness and a roll-off when the pH is higher than $pH=10$.

Regarding previous validation and the conclusions from our adapted model, the next part of this paper presents a comprehensive comparison of five common materials in use in microelectronic applications (Al_2O_3 , Ta_2O_5 , HfO_2 , ZrO_2 and Sn_2O_3) using the same method.

3. RESULTS AND DISCUSSION

The previous section showed that the Stern model affords excellent agreement with experimental data. Moreover, this model showed the highest and most stable sensitivity parameters. Therefore, in this section, we report a comparison of five materials common in microelectronic applications (Al_2O_3 , Ta_2O_5 , HfO_2 , ZrO_2 and Sn_2O_3).

An initial objective of the project was to identify a high pH-sensitivity insulator layer (Stern Layer) material based on the surface potential sensitivity parameter. One interesting finding was examining the

influence of the surface potential to pH bulk change. Figure 5 shows that using the adapted model to calculate the theoretical surface potential of (Al₂O₃, Ta₂O₅, HfO₂, ZrO₂ and Sn₂O₃) as a function of pH bulk. The two materials that cover a large space of surface potential are Ta₂O₅ and ZrO₂. What can be clearly seen in this chart is the high rate of response of surface potential when using Tantalum material (Ta₂O₅). Ta₂O₅ rose to a high point and peaked at approximately 0.52 V compared with other materials. Al₂O₃ and HfO₂ revealed a stable surface response to pH bulk change.

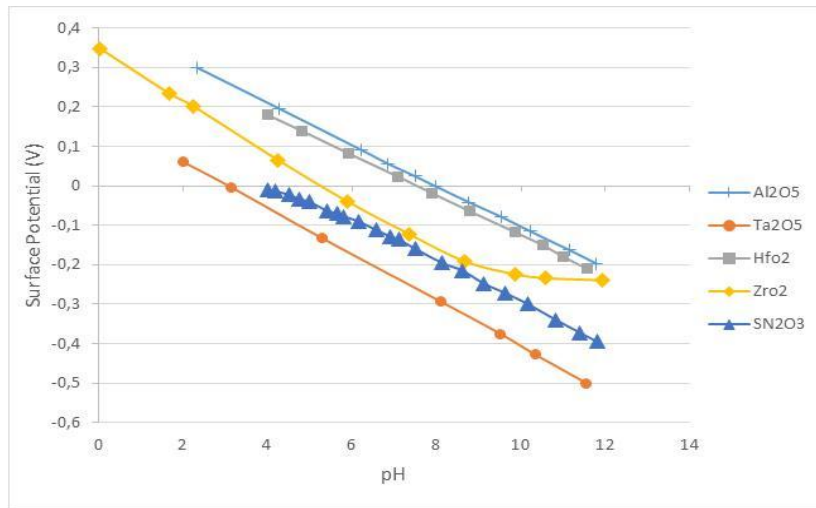


Figure 5. Interface surface potential versus pH relationship

These curves would have been more useful if they had focused on the pH sensitivity value as one of the most important values. These values can remove doubt about which material can achieve the highest sensitivity. Therefore, the calculations of pH-change sensitivity of the five previous high-k materials have been reported based on the adapted model as shown in Figure 6. For more validation, real experimental data gathered from existing literature was compared with theoretical calculations. The experimental data for Al₂O₃ and Ta₂O₅ was collected from [9], HfO₂ from [15], ZrO₂ from [12] and Sn₂O₃ from [10]. The results in Figure 5 are consistent with the data obtained in Figure 4, and confirms that Ta₂O₅ rose to a high point and peaked at approximately 59 mV/pH, within easy reach of the ideal sensitivity (Nernst Limit). ZrO₂ tended towards the next high sensitivity value at around 56 mV/pH. Al₂O₃ and HfO₂ satisfied the same rate at approximately 52 mV/pH. The last one is Sn₂O₃, which theoretically reached around 46 mV/pH. Obviously, these results support previous research into this topic.

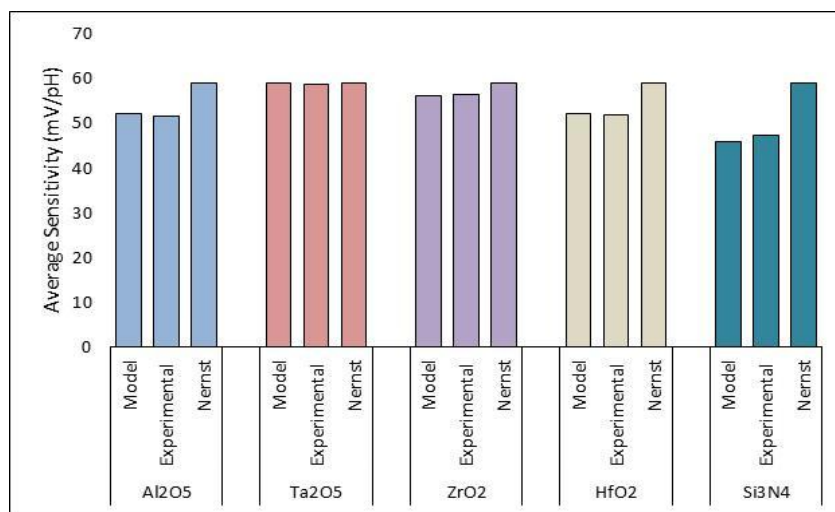


Figure 6. Comparison of the theoretical sensitivities

A comparison of the two results reveals that Ta₂O₅ exhibits the best potential for an ISFET Stern layer. The last step in these findings is to examine the surface potential stability of Ta₂O₅ in terms of the electrolyte concentration change, using Equation (9). Three electrolyte concentrations, 10 mM, 100 mM and 1mM, were used. The results, as shown in Figure 7, indicate that the response of surface potential as calculated by the ISFET model is a little impact by the ionic and electrolyte for different concentrations.

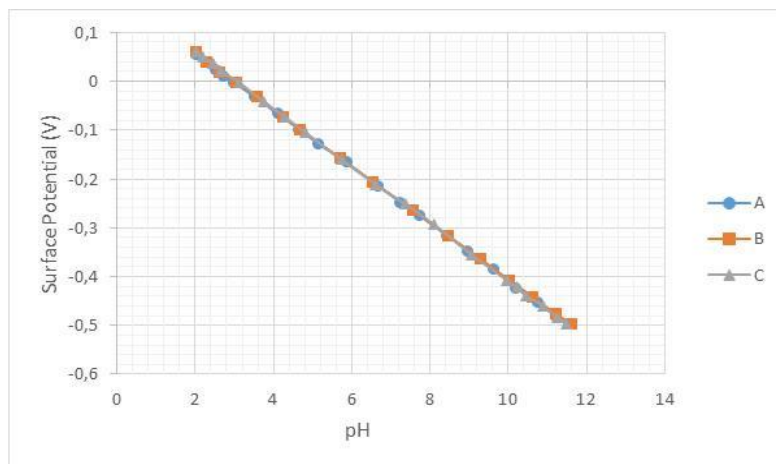


Figure 7. Surface potential of Ta₂O₅ ISFET in (A) 100 mM, (B) 10 mM and (C) 1 mM

4. CONCLUSION

This study set out to identify different high-k materials to use as sensing membranes, rather than using SiO₂. The Gouy-Chapman and Gouy-Chapman-Stern models were combined with the Site-binding model, based on surface potential sensitivity. In summary, the results showed that Ta₂O₅ has a high surface potential sensitivity and exhibits high stability in different electrolyte concentrations. The findings of this research provide insights for examining different materials before going on to expensive real ISFET fabrication. Further research needs to examine more closely the links between IC design simulation and these models for more accurate analysis and further optimisation.

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BIOGRAPHIES OF AUTHORS



Ahmed M. Dinar was born in Baghdad, Iraq in 1984. He received his B. Eng. degree computer engineering from college of Engineering/ Al-Mustanairiyah University in 2007. He received M. Sc degree from Computer Engineering department/University of Technology/Iraq in 2014. Currently, He is a Ph.D. student at Faculty of Electronic and Computer Engineering (FKEKK), Universiti Teknikal Malaysia Melaka since 2017 where his Ph.D. research focuses on CMOS/ISFET sensor for Cancer Detection. he is currently a Lecturer with computer engineering department, University of Technology, Baghdad, Iraq.



A. S. Mohd Zain was graduated B. Eng degree in Electric, Electronic & System from the University Kebangsaan Malaysia. She received the M.Sc. degree in Microelectronics from University Kebangsaan Malaysia and Ph.D. degree in Microelectronics from University of Glasgow United Kingdom. She is a Senior Lecturer at Universiti Teknikal Malaysia Melaka. Her research interests include IC Design for Biomedical Applications and Nanoscale Device Design and Simulation.



F. Salehuddin was received B. Eng degree in communication engineering from the MARA University Of Technology. She received the M.Sc. degree in Microelectronics from University Kebangsaan Malaysia and Ph.D. degree in Microelectronics from Universiti Tenaga Nasional, Malaysia. She is a Senior Lecturer at Universiti Teknikal Malaysia Melaka. Her research interests include Device and Process Simulation of CMOS, Optimization Approach (DOE) and Variability of nanoscale device.