CHAPTER 1

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1.1. Introduction

The increase in urbanization and economic development of the society have brought many changes in the lifestyle of people resulting in less physical activity, unhealthy nutrition, and obesity which leads to many chronic diseases such as diabetes, angina, hypertension, asthma, depression, arthritis, etc. People suffering from such diseases need to go for routine checkup followed by laboratory tests. This has raised the demand and workload on health care systems.

In the direction of solving such problems, point-of-care (POC) devices are very useful. These devices can analyze samples such as blood without the help of laboratory staff. In addition, it provides results in few minutes, which is very much useful and cost effective for people. Many POC devices were developed with the above aim in mind. With such devices people can easily make self-tests at any place and time when necessary and get the results instantly. They can also take online help whether it is necessary to go to a doctor or not. Because of this the number of hospital visits by patients' decreases and the hospitals do not become overcrowded of people having minor problems. The load on doctors reduces and they can get sufficient time for serious patients. The transportation cost and load also reduces a lot. Moreover, the patients save their work time. All these gives rise to an efficient healthcare system. Such portable devices can be very helpful in emergency situations like for treatment in the ambulance, war fields, natural disaster spots, etc.

The POC devices can detect biological materials such as nucleic acids, proteins, pathogens, cells, metabolites, etc. Many metabolites are used as target for POC devices like cholesterol, glucose, acetylcholine, creatinine, urea, uric acid, etc. Different types of both amperometric and potentiometric POC devices have been developed for the detection of various target molecules. The ideal POC devices is composed of three sections:

- The fluidic part where site binding occurs

- Sensitive surface which captures target specifically
- Signal transducer to measure the variations due to site binding

Many of these POC devices are used as biosensors. Last few decades have been very important towards the research and development of biosensors. The first biosensor was developed by Clark in 1962. He developed an amperometric oxygen electrode biosensor by immobilizing it with glucose oxidase enzyme. Since then many variety of ideas were put forward towards the advancement of biosensors with the combined knowledge of various branches of applied science and engineering. Among those ideas, the one that caught the eyes of researchers the most was the combination of enzymes with an ISFET (ion-sensitive FET), called as enzyme modified FET or ENFET. This invention gave a very vast area of research. ENFETs became so popular because of the use of silicon based FET as the basic structure. This helped in miniaturization of devices. A lot more advantages came into light like small size, low weight, fast response, better fabrication and packaging, high reliability, low cost etc. Moreover, it has a vast field of applications like defence, security, drug industries, medicine, etc.

To understand the operation of the ENFETs, theoretical models need to be developed. Modeling is a process by which the objects in the real world can be represented in terms of physical or mathematical equations and parameters. It helps in gathering information about something without its implementation in real life. It is always followed by simulation. Both the terms modeling and simulation are interrelated and equally important. Modeling creates an implementation model of something, which can be executed on a computer. Simulation implies execution of the model. In short one can say, modeling stands at the abstraction platform and simulation stands at the implementation platform of the same system.

Semiconductor device modeling revolves round the creation of models of electrical devices considering their behavior on the basis of the concepts of fundamental physics. A model is formed by considering the mathematical equations using approximation technique on the basis of the qualitative theory. The equations used are derived from the qualitative understanding of the device. The simulation of the model formed can be done by using softwares such as SPICE (Simulation Program with Integrated Circuit Emphasis), MATLAB (MATrix LABoratory), Synopsys, etc.

ISFET modeling came up with the modification over MOSFET modeling. Some equations and parameters are added to the MOSFET model to get the ISFET model. MOSFET is a completely electronic device and it uses the semiconductor field effect transistor principles. But ISFET is an electrochemical device so, both semiconductor field effect transistor principles and chemical calculations are involved in it. If one tries to make a physical model of ISFET, the chemical part is replaced by considering potential difference by certain modeling. Because of this physical model cannot be considered as an exact model for ISFET. For making an exact model, the chemistry part should be considered. Such type of ISFET modeling where both the electronics and chemistry principles are involved is called electrochemical modeling. Many physical models of ISFET have been found but very few electrochemical models.

Immobilization of an enzyme layer on top of ISFET gives ENFET, so, ENFET modeling includes enzymatic reactions and diffusion phenomena leading to pH variations on ISFET's surface in addition with the ISFET electrochemical modeling steps. Few electrochemical models for Si based ENFETs were developed. With the aim of device miniaturization, researchers thought of using high-κ dielectric materials as insulator in the FET devices because scaling of SiO_2 had many limitations. But the compatibility of high-κ dielectric materials with Si has been found to be very low, so, nanomaterials such as graphene and CNT started being used as substrate because of their high compatibility with high-κ dielectrics, leading to further device miniaturization and improved performance. Using high-κ dielectric as insulator and graphene and CNT as substrate materials, few ENFET devices have been fabricated. However, the key scientific and technological problem is that, the electrochemical models for such devices are not available. Such device models are required to understand the device physics, explain experimental data and choose the parameters for the high sensitivity and selectivity of nanomaterial based ENFET devices for bioelectronics applications. Also, it is important to study whether the characteristics of these devices are similar to the traditional Si based ENFET device characteristics or not. This will decide whether the basic theory and principle associated with conventional Si based ENFET devices can be applied to graphene and CNT based devices or not as there is no general accepted theory or principle, which completely describes the physics of graphene and CNT based ENFETs. Moreover, since a

transition takes place from Si domain to graphene or CNT domain, the parameters may be different. Such studies are not available in literature.

In view of the above scientific and technological problems, the research work aims to developed a generalized model for high-κ dielectric and nanomaterial based ENFETs. To fulfill the specific aim, the following objectives have been formulated for the studies embodied in this thesis:

1.2. Objectives

I. To develop a generalized electrochemical model for high-κ dielectric and nanomaterial based ENFETs.

II. To validate the developed generalized electrochemical model with respect to:

   a. Potassium-doped polypyrrole/carbon-nanotube (K/PPy/CNT) based graphene ENFET (G-ENFET) with ZrO_2 as dielectric for cholesterol detection.

   b. Chitosan/nickel oxide (CH/NiO) based carbon-nanotube ENFET (CNT-ENFET) with ZrO_2 as dielectric for acetylcholine detection.

   c. Chitosan/nickel oxide (CH/NiO) based carbon-nanotube dual-gated ENFET (CNT-DG-ENFET) with HfO_2 as dielectric for acetylcholine detection.

To accomplish these objectives, the content of this thesis entitled “Electrochemical modeling and validation of high-κ dielectric and nanomaterial based enzyme field effect transistors (ENFETs) for biomolecule detection” has been divided into the following chapters.

Chapter 1: Introduction

This chapter provides a brief introduction about the origin of the work that motivates to pursue the research work, challenges involved, objectives undertaken and the methodology used to meet the objectives.

Chapter 2: Review of Literature

This chapter describes the theory of MOSFETs, ISFETs and ENFETs, its evolution with time, merits and demerits. It discusses development of different types of ISFET and ENFET models with time and need. The theoretical deductions of various models used for modeling such as Fick's law, Bousse's model, etc. have been discussed in details. A discussion has also been presented on graphene and CNT with focus on its use as semiconductors. Moreover, the biomolecules and enzymes used have been described with their significance.

Chapter 3: A generalized electrochemical model for high-κ dielectric and nanomaterial based ENFETs

This chapter discusses the key steps involved in ENFET electrochemical modeling i.e. modeling of enzymatic reactions, modeling of the diffusion phenomena of substrate and products in the electrolyte, modeling of acid/base reactions of the product in the electrolyte, ISFET and current transport modeling.

Contribution of this work: From the developed generalized model, it was found that the most influential parameters which produce variations in the device performance are K_M, n_{enz}, $[S]$, K_a, pH_{pzc}, pH_0, β, N_s, $V_{TH,ENFET}$, κ, μ, W, L and C_{ox}.

Chapter 4: Electrochemical model for graphene ENFET (G-ENFET) with ZrO_2 as dielectric for cholesterol detection.

This chapter presents an electrochemical model for K/PPy/CNT based G-ENFET with ZrO_2 as dielectric for cholesterol detection. The variations in the traditional model due to use of graphene as substrate have been discussed. The insulating layer of high-κ dielectric ZrO_2 (κ=25) has a thickness of about 10 nm showing good insulating effect even at nanometer range. The K/PPY/CNT in which the enzymes have been immobilized has larger area and lesser thickness of about 100 nm. As a result, it can hold more enzyme and give better response and higher sensitivity. Moreover, the mobility of graphene is very high (about 15000 cm^2/Vs). This also contributes towards the high sensitivity of the device as even very small potential variation at the surface gives a noticeable change in current. The results based on the proposed model have been found to be in good agreement with the experimental results.

Contribution of this work: A good validation of the generalized model with G-ENFET has been presented. It depicts a transition from Si to graphene domain with the same basic theory and principles.

Chapter 5: Electrochemical model for carbon-nanotube ENFET (CNT- ENFET) with ZrO_2 as dielectric for acetylcholine detection.

This chapter presents an electrochemical model for CH/NiO based CNT- ENFET with ZrO_2 as dielectric for acetylcholine detection. The variations in the traditional model due to use of CNT as substrate is discussed. CNT substrate makes the ENFET junctionless. The channel is already present along with source and drain so, the channel inversion potential required in traditional Si-based ENFET devices has been excluded in this device model. Moreover, due to high mobility of CNT, a good amount of current has been obtained at this nano level. The characteristics of the device model have shown good agreement with the fabricated device characteristics.

Contribution of this work: A good validation of the generalized model with CNT-ENFET has been presented. It shows that the basic theory and principle associated with conventional Si based ENFET devices are also applicable to CNT-ENFET devices.

Chapter 6: Electrochemical model for carbon-nanotube dual-gated ENFET (CNT-DG-ENFET) with HfO_2 as dielectric for acetylcholine detection.

This chapter presents an electrochemical model for CH/NiO based CNT-DG-ENFET with HfO_2 as dielectric for acetylcholine detection. The variations in the traditional model due to use of dual gate have been discussed. HfO_2 is a high-κ dielectric with dielectric constant 25 and has thickness of about 10 nm giving good insulating effect and enhanced sensitivity even at nanometer range. The use of ZnO, a low-κ dielectric, as the bottom gate material gives lesser current as compared to the top gate. Because of this, the variation in current mostly occurs because of top gate. The increase in sensitivity of the device with the use of dual gate has been emphasized. The sensitivity of the device from modeling has been found to be about 1.1 V/pH, which is comparable to experimentally determined sensitivity of 1.2 V/pH.

Contribution of this work: It shows that the generalized model can be used for CNT-DG-ENFET with modifications in the current transport model. Also, a good rise in sensitivity beyond Nerstian limit is observed with the use of dual gate.

Chapter 7: Conclusion and future scope

This chapter gives overall conclusions of the research works including major results and highlighting the significant findings obtained from various simulation results reported in this thesis. Future prospects of these works have also been presented.

1.3. Methodologies applied

The proposed research work was planned to proceed in the following phases:

Phase 1: Defining the research problem through a detailed literature survey on ENFETs.

- Literature survey on different types of ENFETs with special focus on high-κ dielectric and nanomaterial based ENFETs.
- Detailed study on the types of ENFET modeling – physical modeling and electrochemical modeling.
- Finding the values of parameters used in modeling.

Phase 2: Identifying the key steps involved in ENFET electrochemical modeling.

- Modeling of enzymatic reactions.
- Modeling of the diffusion phenomena of substrate and products in the electrolyte.
- Modeling of acid/base reactions of the product in the electrolyte.
- ISFET modeling.
- Current transport modeling.

Phase 3: Developing a generalized electrochemical model for high-κ dielectric and nanomaterial based ENFETs.

- Determination of values of the parameters used in modeling.

- Modeling the changes in the electrochemical model with the use of nanomaterials.
- Effect on sensitivity with the use of high-κ dielectrics.

Phase 4: Validating the developed generalized electrochemical model with respect to K/PPy/CNT based G-ENFET with ZrO_2 as dielectric for cholesterol detection.

- Simplifying the generalized electrochemical model for cholesterol detection using G-ENFET.
- Plotting the I-V characteristic for the model and compare with the fabricated device characteristics for different cholesterol concentrations.

Phase 5: Validating the developed generalized electrochemical model with respect to CH/NiO based CNT- ENFET with ZrO_2 as dielectric for acetylcholine detection

- Simplifying the generalized electrochemical model for acetylcholine detection using CNT-ENFET.
- Plotting the I-V characteristic for the model and compare with the fabricated device characteristics for different acetylcholine concentrations.

Phase 6: Validating the developed generalized electrochemical model with respect to CH/NiO based CNT-DG-ENFET with HfO_2 as dielectric for acetylcholine detection.

- Simplifying the generalized electrochemical model for acetylcholine detection using CNT-DG-ENFET.
- Plotting the I-V characteristic for the model and compare with the fabricated device characteristics for different acetylcholine concentrations.
- Determining the effect on sensitivity with the use of dual gate.