Abstract

Non-Stoichiometric Titanium-Oxide Gate Electrodes for EGFET Based pH Sensors †

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Abstract: A compact pH measuring electrochemical sensor module was developed for Smart Multi-Well Plates (SMWP) applicable for highly parallelized cell culture analysis using incorporated Organ-on-Chip devices. A specific electronic architecture was designed and manufactured containing an extended gate field effect transistor as the transducer device. Electrochemical electrodes were functionalized using pH sensitive metal-oxides and applied as the gate material. The composition and the related pH sensitivity of differently deposited materials were characterized and the suitability of ALD-deposited, non-stoichiometric titanium oxide (TiO_x) for sensitive pH measurement was verified showing excellent responses close to the ideal Nernstian slope (59 mV/pH).

Keywords: pH sensor; extended gate FET; metal-oxide; non-stoichiometric titanium oxide; TiO_x

1. Introduction

Besides different marker molecules—such as relevant amino acids, carbohydrates, and drugs such as antibiotics—pH is another important parameter used to characterize the metabolic parameters of cell cultures and tissues in Organ-on-Chip applications. The good performance of the optical analysis method for pH measurement in Phenol red indicator-dye-containing media was proven, although a generally used, integrated electrochemical method could be more beneficial for various culture media.

Miniaturized and robust pH detectors based on potentiometric, conductometric methods or ion-selective field effect transistors (ISFET) and extended gate field effect transistors (EGFET) have been demonstrated utilizing various ion-sensitive metal-oxide (MO_x) materials such as RuO_2, IrO_2, TiO_2, SnO_2, Ta_2O_5, WO_3, ZnO, etc. In the case of the ISFET and EGFET pH sensors, the source–drain current of the transistor is controlled by the electrostatic field generated by the ion-sensitive material covered gate electrode.

The pH sensitivity of the gate materials can be explained by the surface charging of the metal-oxides, mainly due to the specific adsorption of H^+/OH^- ions and protonation and deprotonation reactions evolving at surface sites. The MO_x sensing layer can be fabricated by screen printing, vacuum sputtering, and sol–gel or electrodeposition methods and characterized mainly by potentiometry, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) to define their sensing performance [1].

In this work, titanium-oxide layers with different compositions were deposited using alternative techniques, analyzed, and compared as potential sensitive materials of an EGFET-based pH sensor.

2. Materials and Methods

Electrochemical electrodes including integrated Pt reference/counter electrodes and comb-like metal-oxide working electrodes with Pt or Au contacts were manufactured on Borofloat^{TM} glass substrate (Figure 1c). The Pt and Au metal layers were deposited by vacuum sputtering and vacuum evaporation, respectively. Titanium-oxide layers were deposited by vacuum sputtering and atomic layer deposition (ALD) at 300 °C and 100 °C so as to be compatible with the applied heat-sensitive materials. The metal wires and MO_x layers were patterned by lift-off lithography. The different MO_x layers were analyzed using X-ray Photoelectron Spectroscopy (XPS) to determine their specific composition. The MO_x-functionalized electrochemical electrodes were connected as an extended gate in the proposed EGFET-based circuit represented in Figure 1a,b and the performance of the system was tested as demonstrated in Figure 1d.
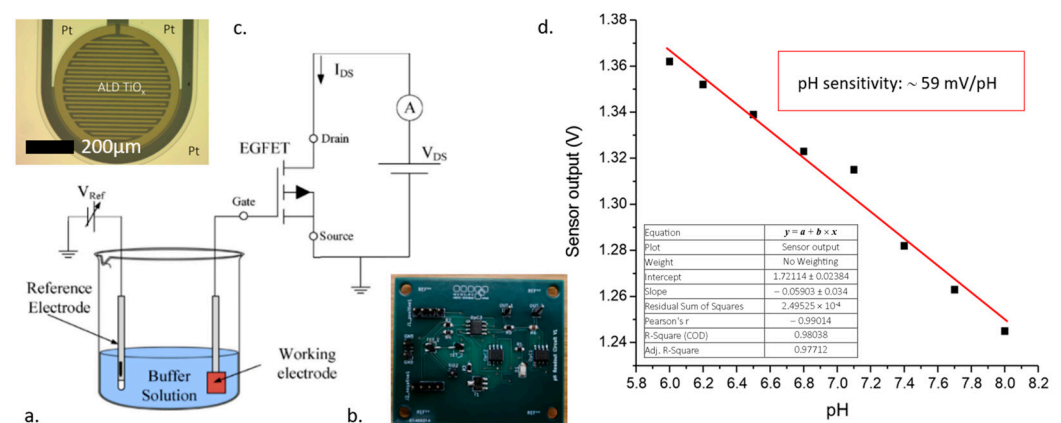

Figure 1. Schematic measurement setup representing the electronic architecture of EGFET-based pH sensor (**a**), the manufactured read-out electronics (**b**), and the MO_x-functionalized working electrode (**c**). The pH sensitivity of the non-stoichiometric TiO_x layer was close to the Nernstian response (**d**).

3. Discussion

The pH sensitivity of the EGFET-based circuit containing different MO_x materials was characterized using pH calibration solutions between 6 and 8 pH values. The differences between the pH sensitivities of various titanium-oxides can be explained by the material structures and compositions. The TiO_2 layers deposited by sputtering and ALD at 300 °C showed moderated pH sensitivity according to their perfectly stoichiometric, inert structure. The TiO_x layer deposited by ALD at 100 °C proved to be perfectly applicable for pH sensing applications, having a close-to-Nernstian 59 mV/pH response (Figure 1d). The surface analytical methods also confirmed that the low-temperature, ALD-deposited titanium-oxide layer is non-stoichiometric and has a Ti:O 1:1.65 atomic ratio.

Author Contributions: In this work, Z.S. was responsible for the design of EGFET-based read-out electronics; Z.S. and L.B. implemented the experimental characterization; S.S., O.H., A.S., C.D. and Z.B. contributed to the development of the ALD process and the analysis of the layers; and P.F. designed the electrode system and the system architecture. All authors have read and agreed to the published version of the manuscript.

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Reference

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