Basis for a biomechanical ‘field-effect-transistor’ mechanism using organic monolayers on silicon(111) revealed by electrical impedance spectroscopy

T C Chilcott, H G L Coster and E L S Wong
School of Chemical and Biomolecular Engineering
terry.chilcott@sydney.edu.au

Abstract. The width of the depletion layer in a silicon wafer and the thickness of an undecanamine organic monolayer covalently attached to the silicon surface was monitored using electrical impedance spectroscopy (EIS) as a function of the bias voltage \( V \) applied between the monolayer surface and the base of the wafer. The dependence of the depletion layer width on \( V \) was analogous to that dependency in a conventional field-effect-transistor (FET) in the range \( 800 \text{mV} > V > -185 \text{mV} \) and consistent with the monolayer performing the function of a FET insulating gate. Decreases in the monolayer thickness of approximately 4 Å were correlated with approximately 100-fold increases in depletion layer width for fixed \( V \) in the range of \(-185 \text{mV} > V > -800 \text{mV} \). This illustrates that changes in thickness induced by the immobilization of important biological molecules targeted by reactive groups incorporated into such a monolayer, could also induce field effects with similar amplification potential to the conventional FET. Thus bio-recognition in a FET-biosensor could occur directly via the mechanics of immobilization rather than indirectly via post immobilization electrochemistry that electrically induces the field effect and is highly dependent on biochemical conditions.

1. Introduction
The principal obstacle to the realization of sophisticated devices for sensing, stimulating and mimicking numerous functions performed by biological systems is the long-term robustness of the interface that links biological processes in aqueous environments to electronic circuitry. The interface formed with metals are plagued by notoriously unstable ionic double layers of high impedance that persist even after surfaces are plied with carbon based monolayers to resist corrosion and contamination [1]. Further, the oxide layer on silicon impedes transduction of biological signals.

Present research is directed towards attaching monolayers directly to the hydride-terminated silicon substrate via formation of robust Si-C bonds [2] which facilitates fabrication of monolayer surfaces terminated with reactive groups that can immobilize biologically recognizable molecules. Such biosensors are of special interest because transduction of the immobilization event can occur via an electric field effect similar to that which underlies the amplification mechanism of field effect transistors (FETs) [3] in which the FET gating is evoked electrochemically by a secondary process that is highly dependent on the pH of the biological environment, after immobilization.

Here, mechanical activation of a field effect response is reported for an organic monolayer on silicon that illustrates that direct detection of the immobilization event can occur independently of the pH and chemistry of the biological environment.
Figure 1. High resolution Inphaze impedance spectrometer and (a) schematic of the characterization chamber illustrating the three-terminal configuration for characterizing (b) functionalized surfaces on substrates and specifically (c) the field-effect-transistor (FET) construct of an undecanamine monolayer on low-doped silicon. Residue lin-spectra reveal a widening of the FET depletion layer arising from a transition in the gate (monolayer) thickness of (d) $1.2 \times 10^{-9}$ m (---) to (e) $1.6 \times 10^{-9}$ m (----) at a constant gating voltage $V$ of -230 mV.
2. Materials and Methods

Undecanamine monolayers were prepared according to Böcking et al [4]. Si(111) wafers (n-type, 2-8Ωcm) were cleaved into 15 mm square pieces, cleaned in concentrated H₂SO₄:30% H₂O₂ (3:1, v/v) and rinsed in MilliQ water. Hydrogen terminated Si(111) surfaces were prepared by etching in a deoxygenated 40% solution of NH₄F. Silicon pieces were placed into a Teflon holder inside a custom made reaction chamber with a quartz glass window and backfilled with argon. tert-butoxycarbonyl-protected ω-aminoalkene was injected onto the Si-H terminated surface and irradiation with UV light for 2-3h and rinsed several times with hexane, dichloromethane, tetrahydrofuran and ethanol and blown dry under a stream of nitrogen. The tertbutoxycarbonyl (t-Boc) protecting group was removed by treatment with 25% TFA in dichloromethane for 60 min followed by immersion in 10% NH₄OH for 2-3 min to obtain a surface terminated with unprotonated amino groups.

Gallium-indium eutectic was applied to the underside of silicon pieces to form a low-ohmic contact with the working electrode of the Inphaze characterization chamber shown in figure 1(a). A gearing mechanism regulated by springs (not shown) delicately lowered the gasket of rectilinear cross-section onto the functionalized surface to seal a precisely defined ‘active’ area of 1.81x10⁻⁵ m² while minimizing distortion of the surface at the gasket perimeter. A 100 mM KCl electrolyte wetted the ‘active’ surface, the counter electrode and the recessed reference electrode (type LF-2 from Innovative Instruments Inc. 8533 Queen Brooks Ct. Tampa, FL 33637, USA). The counter and working electrodes injected sinusoidal current i of angular frequency ω through the surface while the reference electrode monitored the voltage response v. The amplitude of v divided by that of i yielded the impedance magnitude and the phase of v referenced to that of i yielded the impedance phase ϕ. The conductance and capacitance are given by cos(-ϕ)z and sin(-ϕ)/ωz, respectively. The Inphaze chamber design includes special features [5] for ensuring a uniform density of i that enables full utilization of the 24-bit acquisition of v that yields better than 1/1000 degrees resolution in ϕ at values of ω as low as 1/1000 Hertz [6]. Angstrom resolutions of substructures on silicon [7] and gold [8] have been achieved.

3. Results and Discussion

Figure 2 depicts two quasi steady state capacitance and conductance spectra for the undecanamine monolayer on silicon at a fixed bias. Maxwell-Wagner models fitted to the spectra are shown in figure 2(c). The conductance and capacitance values for the 1st Maxwell-Wagner element, i.e. g₁ and c₁, are consistent with the known properties of the electrolyte. Those values for the 7th element yield thickness values (d=ɛₑɛᵣ/c₁) consistent with those expected for a monolayer comprised principally of hydrocarbon chains of dielectric constant ɛₑ=2 (ɛᵣ=8.85x10¹² F/m). The 4x10⁻⁷m transition in thickness from one quasi state (●) to the other (●) is consistent with the reported range of likely canting angles for the undecanamine molecules in such a monolayer [4]. Further, the conductivity values (i.e. σ=g₁d₁) are consistent with those expected for such a monolayer and for an insulating gate of a FET, e.g. the silicon dioxide layer in a metal-oxide-silicon-field-effect-transistor (MOSFET).

The transition in monolayer thickness correlates with changes in the properties of the 2nd, 3rd, 4th, 5th and 6th elements shown in figure 2(c), which can only be attributed to sub-layers induced in the silicon by the field effect. The depth of penetration of the effect is illustrated in the Residue line-spectra shown in figures 1(d) and 1(e). The line-spectrum in figure 1(d) is that for a monolayer thickness of 12Å (——) and reveals that sub-layers with the lowest frequency constant values, given by f=ɛₑ/(2πɛᵣ), and hence those corresponding to sub-layers of lowest conductance, are consistent with the known properties of a depletion region. Figure 1(e) illustrates that a 4Å increase in the monolayer thickness (∆) was correlated with increases in the thicknesses of most of the silicon sub-layers resulting in an approximate 100-fold widening of the depletion region to approximately 0.1µm.

This illustrates that the field effect can be induced to a similar extent either physically or electrically. Further, the physical change and the associated field effect are of suitable magnitude for the transduction of the mechanics of immobilization of biologically recognizable molecules to the functionalized surface of an organic gate in a field effect transistor.
Figure 2. Measured dispersions of (a) the capacitance and (b) conductance with frequency $\omega$ of the undecanamine monolayer on low doped silicon for a bias potential $V$ fixed at -230 mV. (c) Maxwell-Wagner circuit elements fitted to the measured dispersions.

References

[1] Cornell, B.A. et al. (1999) US patent PN 5,874,316 (February 23 1999)
[2] Sieval, A.B., Linke, R., Zuilhof, H., Sudholter,. E J.R. (2000) Advanced Materials 2000, 12, 1457-1460
[3] Patolsky, P, Lieber, C.M. (2005) Materials Today, April issue 20-27
[4] Böcking T, James M, Coster HGL, Barrow KD and Chilcott TC (2004) Langmuir 20(21) 9227-9235
[5] Coster, H.G.L, and Chilcott, T.C., (2007) “Apparatus for electrochemical characterisations” PCT application filed in Germany(2006), internationally (2007)
[6] Coster, H.G. L. and Chilcott, T. C. (2006) “An improved method of measuring the phase difference between arbitrary periodic waveforms.” PCT application filed in Australia.(2006)
[7] Chilcott, T.C., Wong, E.L.S., Böcking, T. and Coster, H.G.L. (2008) Physiol. Meas. (29), S307–S319
[8] Chilcott , T.C., Wong, E.L.S., Coster, H.G.L., Coster, A.F.C. and James, M. (2009) Electrochimica Acta 54, 3766-3774