

Characterization of Electron Conduction in Unsaturated Organic Monolayers on Silicon(111) using Electrical Impedance Spectroscopy

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Abstract— Electrical impedance spectroscopy (EIS) studies of monolayers comprised of molecules of *Geranyllinalool* and *Isophytol* revealed structural and molecular organizational details that were compatible with crystallographic dimensions of these molecules. *Geranyllinalool* (C₂₀H₃₄O) and *Isophytol* (C₂₀H₄₀O) differ principally in the structures of their hydrocarbon backbones. Several carbon-carbon bonds in the *Geranyllinalool* backbone are double bonds (unsaturated) whereas those bonds in *Isophytol* are single (saturated). Even though the *Geranyllinalool* monolayers were thicker than the *Isophytol* monolayer, EIS further revealed that their conductivities were an order of magnitude higher than those of the *Isophytol* monolayers. This is consistent with the electron enriched double bonds in the *Geranyllinalool* backbone providing a better conduction path than the electron depleted single bonds in the *Isophytol* backbone. The study reveals that unsaturated organic monolayers can improve the electrical connectivity of the semiconductor-biological interface whilst maintaining biocompatibility and passivity.

Keywords— biosensors, monolayers, impedance, silicon, electron conduction.

I. INTRODUCTION

The future of biosensor and stimulatory electrodes lies in improving the interface between conventional electronics and targeted biological events.

Conventional electronics utilizes semiconductors (silicon) and metals (e.g. gold) which electrically interact with each other via electron conduction but neither interacts as directly with the bulk aqueous biological environment where conduction is ionic. Silicon oxidizes to form a layer of SiO₂ whereas gold forms an “ionic double layer” in which ions form one layer in the aqueous phase and electrons form the other layer in the gold. Although the “ionic double layer” and the SiO₂ layer are only nanometers in thickness, they are very poor conductors of both electrons and ions. Neither provides the means of sensing biologically based electron transfers.

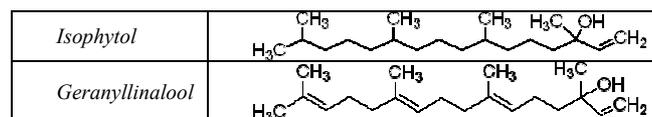
Successful detection of DNA-mediated electron transfers (see [1] and [2]) have been possible on gold but only after the interface was functionalized with single-stranded DNA probes distributed in an otherwise biologically passivated organic monolayer [3]. EIS unambiguously correlated an 8-

fold increase in conductance with DNA-mediated electron transfers. Substantial capacitive changes, that were indicative of structural and/or dielectric variations arising from the formation of the double helices, were also correlated with the transfers. However, a specific characterization was complicated by the persistence of a modified ionic double layer and effects arising from the rough surfaces of gold.

Here we present an EIS study of electron transfers in organic monolayers attached directly to atomically flat silicon (i.e. no SiO₂ layer) without the complications associated with gold and the use of biologically incompatible ferric cyanide as an electro-catalyst in the aqueous phase [4].

The EIS study establishes procedures for studying structural and functional features of functionalized monolayers, such as those that facilitate DNA-mediated electron transfers.

Table 1 Molecular structure of *Isophytol* and *Geranyllinalool* highlighting the different types of carbon-carbon bonding in the hydrocarbon backbones



II. EXPERIMENTAL

A. Silicon-Carbon Chemistry

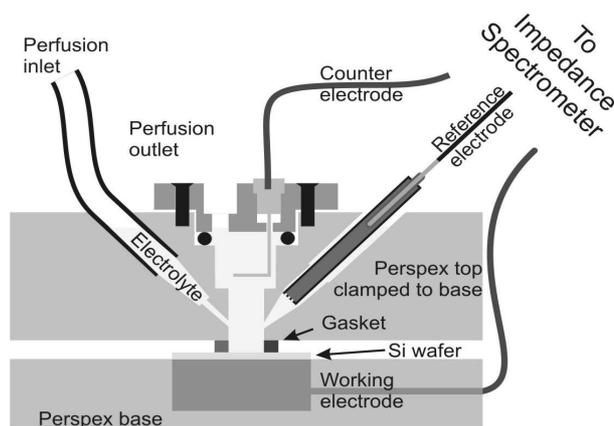
Methods of attachment of organic monolayers to silicon are described in detail elsewhere [5]. Highly doped Si(111) wafers (0.01-0.1 Ωcm) were cleaned in “Piranha” solution at 90°C for 30 min and rinsed thoroughly with Milli-Q water and then etched in deoxygenated NH₄F solution for 20 min to generate hydride terminated Si(111) surfaces. The freshly etched surfaces were then converted to a Si-C linked monolayer through hydrosilylation in deoxygenated solutions of either *Geranyllinalool* or *Isophytol* by photochemical activation under UV light for 2-10 hours. The functionalized silicon wafers were then rinsed with hexane, dichloromethane, tetrahydrofuran and ethanol prior to drying thoroughly under a stream of nitrogen.

B. Electrical impedance measurements

Impedance measurements were performed with an Inphaze Impedance Spectrometer (Inphaze Pty Ltd., Sydney, Australia) over a frequency (ω) range of 6 mHz to 100 kHz using the Inphaze 3-electrode electrochemical cell (Fig. 1). Gallium-indium eutectic was applied to the non-functionalized side of the wafer which was then placed on the working electrode where a low-ohmic contact was formed.

Ac electric current used for impedance measurements was injected into the wafer via the working electrode and the counter electrode immersed in a 100mM KCl electrolyte that also made contact with the functionalized surface of the wafer. A Ag|AgCl reference electrode (type LF-2 from Innovative Instruments Inc. 8533 Queen Brooks Ct. Tampa, FL 33637, USA) was located in an electrolyte filled recess in the chamber and monitored the electric potential response of the system to the *ac* current.

The chamber also featured a mechanism for sealing a precisely defined area of the functionalized surface while minimizing deformation of that surface. The significance of the rectilinear gasket and recessed reference electrode are described in detail elsewhere ([6], [7]).



A systematic study of alkyl (saturated) monolayers of hydrocarbon chain length ranging from 10 to 18 carbons [8] has provided accurate estimates of the thicknesses of these layers using electrical impedance spectroscopy (EIS) and X-ray reflectometry (XRR) to better than an Angstrom resolution. The EIS estimates were based on measurements of the capacitance per unit area, C , of the layer in contact with a KCl electrolyte, in which the thickness is given by;

$$d = \epsilon_r \epsilon_0 / C \quad (1)$$

where ϵ_r is the dielectric constant of the layer (≈ 2.05) and ϵ_0 is the permittivity of free space ($= 8.85 \times 10^{-12} \text{ Fm}^{-1}$).

The conductance measurements for these layers were consistent with them acting as an insulator between the silicon and electrolyte.

III. RESULTS AND DISCUSSION

The impedance data of the monolayer-electrolyte systems are shown in Fig 2 as dispersions of the conductance and capacitance with frequency ω . The dispersion for both the *Geranyllinalool* and *Isophytol* systems converge at high frequencies yielding the conductance and capacitance values for the electrolyte (1st circuit element shown in Fig. 3).

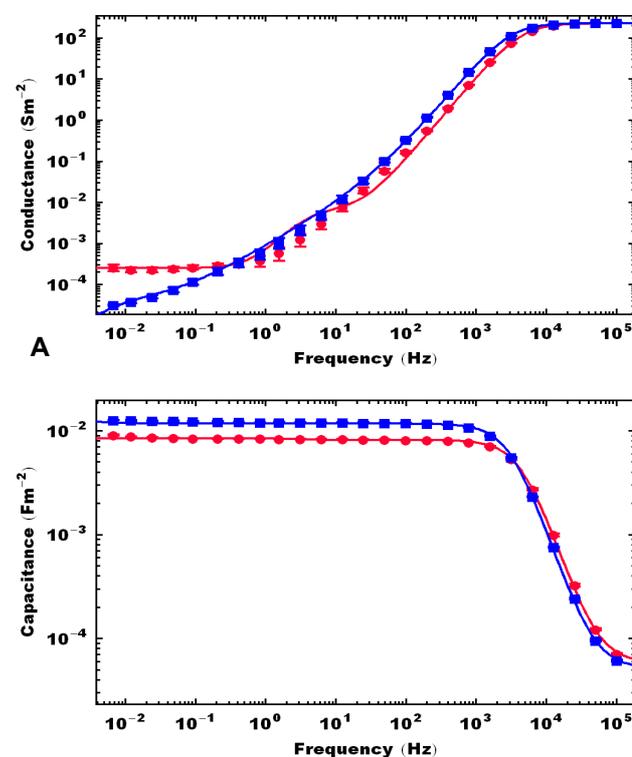


Fig. 2 Conductance (A) and capacitance (B) dispersions with frequency obtained from the impedance measurements of *Geranyllinalool* (●) and *Isophytol* (■) monolayers in contact with a 100mM KCl electrolyte. Convergence of data at high frequencies yields properties of the electrolyte whilst divergence at low frequencies reveals differences in properties of the monolayers.

The dispersions diverge at low frequencies revealing different conductive and capacitive properties of the *Geranyl-*

linalool (●) and *Isophytol* (■) monolayers. A Maxwell-Wagner model was readily fitted to the *Geranyllinalool* (●) data (Fig 3A). However, the divergence of the conductance data for the *Isophytol* (■) monolayers at very low frequencies (see Fig. 2A) could only be explained by a frequency (ω) dependent conductance element (g_3 in Fig. 3B). However, the capacitance dispersion in this frequency range was independent of frequency (see Fig. 2B) and yielded a capacitance value for the *Isophytol* monolayer (c_3 in Fig. 3B) that was independent of frequency.

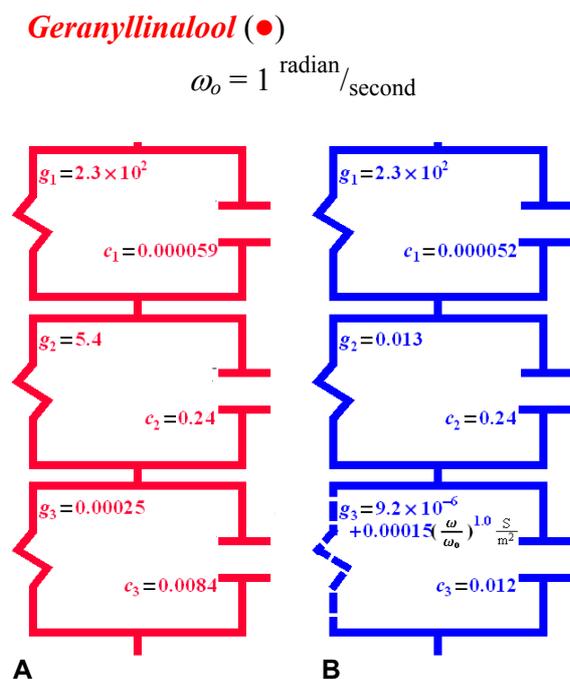


Fig. 3 Circuit diagrams for generating theoretical curves shown in Fig. 2 for the *Geranyllinalool* (A) and *Isophytol* (B) monolayer-electrolyte systems. The 1st circuit element yields conductance (g_1) and capacitance (c_1) values for the bulk electrolyte that are constant in frequency. The 3rd circuit element reveals capacitance values (c_3) that are constants in frequency for both monolayers. Whilst the conductance value (g_3) for the *Geranyllinalool* monolayer is also constant the conductance value for the *Isophytol* (B) monolayer includes a frequency (ω) dependent component. The 2nd circuit element is attributed to an interfacial layer between the electrolyte and monolayer.

An additional Maxwell Wagner element (2nd circuit element in Fig. 3) was required to fit the conductance and capacitance dispersions with frequency at mid-frequencies. Its electrical properties are indicative of an interfacial layer between the electrolyte and monolayer but are such that the layer does not contribute substantial to the total impedance of the systems, especially at low frequencies where electri-

cal properties are indicative of the low conducting monolayers.

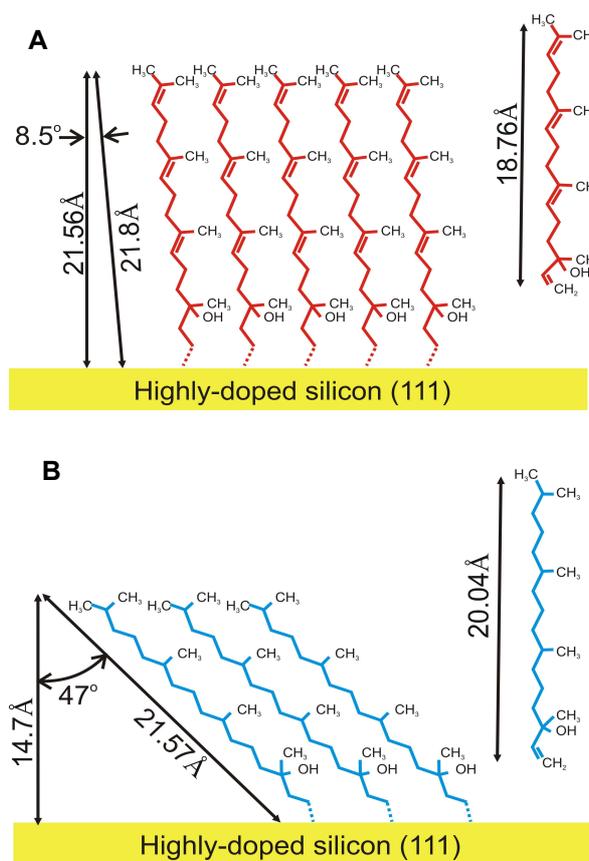


Fig. 4 Schematic of structures for *Geranyllinalool* (A) and *Isophytol* (B) monolayers. Thicknesses of the monolayers were estimated from the capacitance values obtained for the 3rd circuit elements shown in Fig. 3, assuming a dielectric constant of 2.05. Molecular dimensions are based on crystallographic studies and take into account reorientation of terminal groups upon reacting with the silicon.

The capacitance values for the monolayers (3rd circuit element in Fig. 3) provide a means of estimating the thicknesses of the layers using Eqn. 1. Schematics of the layers based on these thickness values and molecular lengths based on crystallography [9] are depicted in Fig. 4. These indicate that the *Geranyllinalool* molecules in the monolayer stand almost vertically whereas the *Isophytol* (B) molecules are orientated at an angle of approximately 47° to the normal. These canting orientations are consistent with expectations that the double C-C bonds in the *Geranyllinalool* molecule would result in a more rigid hydrocarbon backbone than one

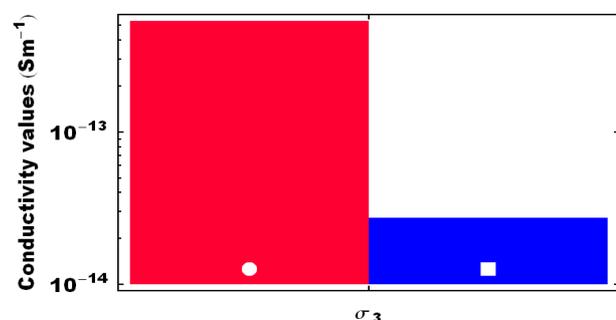
comprised exclusively of single bonds such as the backbone of the *Isophytol* molecule.

Another expectation is that the electron rich double bonds in a backbone would also enhance electron transport through the monolayer. Indeed a comparison of the conductance values for the 3rd circuit in Fig. 3 (i.e. g_3) reveals that the conductance of the *Geranylinalool* monolayer is at least an order of magnitude larger than the conductance of the thinner *Isophytol* monolayer.

The conductivities of the monolayers provide a comparison of the electron transference properties that is independent of the monolayer geometries. Conductivity in the “one-dimension” experimental system used in this study is given by;

$$\sigma_3 = g_3 d_3 \quad (2)$$

which yields a substantially larger conductivity value for the unsaturated monolayer as depicted in Fig. 5.



IV. CONCLUSIONS

Electrical impedance spectroscopy facilitates precise characterizations of structural and functional features of functionalized monolayers that have been attached directly to atomically flat silicon.

Such characterizations can proceed without complications associated with oxidized layers, ionic double layers, rough surfaces and electro-catalysts in the aqueous phase.

Unsaturated organic molecules substantially enhance electron transfers.

Future work will explore roles that unsaturated organic molecules can play in coupling conventional electronics (silicon semiconductors) to targeted biological events.

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