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Characterisation of alkyl-functionalised Si(1 1 1) using reflectometry and AC impedance spectroscopy

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Abstract

The past few years have seen a dramatic increase in the study of organic thin-film systems that are based on silicon–carbon covalent bonds for bio-passivation or bio-sensing applications. This approach to functionalizing Si wafers is in contrast to gold-thiol or siloxane chemistries and has been shown to lead to densely packed alkyl monolayers. In this study, a series of alkyl monolayers $[CH_3(CH_2)_nCH{=}CH_2; n = 7, 9, 11, 13, 15]$ were directly covalent-linked to Si(1 1 1) wafers. The structures of these monolayers were studied using X-ray reflectometry (XRR) and AC impedance spectroscopy. Both techniques are sensitive to the variation in thickness with each addition of a CH_2 unit and thus provide a useful means for monitoring molecular-scale events. The combination of these techniques is able to probe not only the thickness, but also the interfacial roughness and capacitance of the layer at the immobilized surface with atomic resolution. Fundamental physical properties of these films such as chain canting angles were also determined.

Keywords: X-ray reflectometry; AC impedance spectroscopy; Self-assembled monolayer; Thin film

1. Introduction

Molecular self-assembly is a powerful approach for producing novel nanoscale architectures at the solid surfaces. To date self-assembled monolayers (SAMs) utilizing thiol-bonds to gold and organosilanes on silica surfaces have been used extensively for the controlled immobilisation of biomolecules. Regardless of the substrates and strategies being used to form SAMs a detailed understanding of the structure, molecular packing, and surface termination of these films is essential for understanding the relationships between microscopic structure and macroscopic chemical and physical properties. Different analytical techniques, including X-ray photoelectron spectroscopy (XPS) [1], ellipsometry [2], transmission electron microscopy (TEM) [3], atomic force microscopy (AFM) [4,5] and scanning tunneling microscopy (STM) [6,7] have been used and provide an excellent basis for the understanding of the structure, order and bonding of SAMs. Nevertheless, the ability to monitor the effect of changes in molecular structure at the SAMs upon biorecognition events is also vital to give an insight to the fundamental chemistries taking place at the interface.

In this study, we apply the scattering technique of X-ray reflectometry (XRR) and the electrochemical technique of AC impedance spectroscopy to investigate a series of alkyl monolayers $[CH_3(CH_2)_nCH{=}CH_2; n = 7, 9, 11, 13, 15]$, which were covalently bonded to the surface of Si(1 1 1) wafers. Henceforth these will be referred to as C10, C12, C14, C16, and C18 organic monolayers. Both XRR and AC impedance techniques are non-destructive and non-contact techniques; however the XRR is performed in the air while the impedance measurements are performed in aqueous solution. Our objective is to take advantage of the high surface sensitivity of both techniques to show that complementary information, such as the thicknesses of these monolayers can be obtained with angstrom precision.

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2. Experimental procedure

2.1. Materials

Reagent grade 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, potassium chloride, dichloromethane and methanol were purchased from Aldrich Chemicals (Sydney, NSW, Australia). Hydrogen peroxide, concentrated sulphuric acid and absolute ethanol were purchased from Ajax (Sydney, Australia). 40% ammonium fluoride was obtained from Kanto Kagaku Singapore Pty Ltd. (Singapore). All the chemicals were used as received without further purification. Milli-Q (18 MΩ cm) was used for the rinsing and preparation of solutions.

2.2. Preparation of Si–C linked monolayers

Highly doped Si(1 1 1) wafer pieces (n-type, 0.01–0.1 Ω cm) were cleaned using "Piranha" solution (concentrated H_2SO_4:30% H_2O_2, 3:1, v/v) at 90 °C for 30 min and rinsed thoroughly with Milli-Q water. Caution: piranha solution is highly oxidizing and should be used with extreme care. The process of surface functionalisation of Si wafers by *n*-alkenes follows the method by Sieval et al. [8] and is summarised in Scheme 1 and proceeds as follows. The hydrogen-terminated Si(1 1 1) surfaces were prepared by etching the cleaned Si(1 1 1) wafer in deoxygenated 40% ammonium fluoride solution for 20 min. The 40% ammonium fluoride solution was deoxygenated by bubbling with nitrogen for 30 min. The freshly etched Si(1 1 1) wafers were then functionalized by hydrosilylation *via* thermal activation in neat alkene solution. The neat *n*-alkene (liquid) was deoxygenated by bubbling with nitrogen for 30 min and was placed into a Schlenk flask. The freshly etched Si(1 1 1)-H wafer was then added and the flask heated in an oil bath for 3 h at 200 °C under vacuum (2 mbar). After the reaction the cooled flask was opened to the atmosphere and the functionalized silicon wafer was rinsed with hexane, dichloromethane, tetrahydrofuran and ethanol and dried thoroughly under a stream of nitrogen.

2.3. X-ray reflectometry

X-ray reflectivity curves were acquired using a Panalytical Ltd. X'Pert Pro diffractometer in reflectometer mode. Cu Kα ($\lambda = 1.5406$ Å) radiation produced from a (45 kV) tube source was focused with a Göbel mirror, collimated with pre-and post-sample slits, and detected using a NaI scintillator detector. Reflectivity data are presented as a function of momentum transfer $Q_z = 4\pi \sin\theta/\lambda$, where λ is the X-ray wavelength and θ the angle of incidence onto the sample. Data were collected over the range $0.03° \leqslant \theta \leqslant 5.00°$ in 0.01° steps with counting times of 20 s per step. The Parratt32 software [9] was used to fit model parameters to measured sets of X-ray reflectivity data with a constant background correction. Low frequency oscillations (Kiessig fringes) were observed as expected for a Si surface functionalized by an organic monolayer, which are normally observed for a surface modified with a thin film on a solid substrate.

2.4. AC impedance measurements

AC impedance measurements were performed using an INPHAZE Pty Ltd impedance spectrometer. The 3-terminal measurements were carried out using a 3-electrode system in 100 mM potassium chloride solution, with Ag|AgCl as the reference electrode, platinum as the counter electrode and functionalized Si(1 1 1) wafer as the working electrode. Gallium–indium eutectic was applied to form a rear ohmic contact to the silicon wafers. For the current experiments, the capacitances of the SAMs were measured at a frequency of 0.558 Hz. It has been established from previous studies [10–12] that at this frequency the measured capacitance reflects the capacitance of the layer with the lowest conductance; the strong dispersion in capacitance due to the electrolyte in series with the sample does not manifest for frequencies below ~1000 Hz. The low frequency capacitance is related to the thickness, *d*, of the layers by:

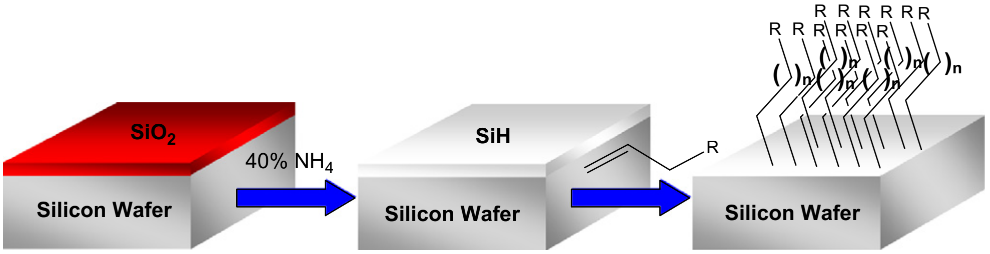
$$d = \frac{\varepsilon_l \varepsilon_o}{C},$$

where ε_l is the dielectric constant of the organic layer, ε_o is the permittivity of free space ($=8.85 \times 10^{-12}$), C is the capacitance per unit area.

3. Results and discussion

3.1. XRR measurements

Observed (crosses) and fitted (solid lines) XRR curves for a series of Si(1 1 1) surfaces functionalized with C10, C12, C14, C16, and C18 covalently-linked monolayers



Scheme 1. Schematic representation of the reaction of 1-alkene with a hydrogen-terminated silicon surface.