Thin Solid Films 519 (2011) 2817–2820

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

In-situ monitoring of alkanethiol self-assembled monolayer chemisorption with combined spectroscopic ellipsometry and quartz crystal microbalance techniques

K.B. Rodenhausen [a,b,*], B.A. Duensing [c], T. Kasputis [c,d], A.K. Pannier [c,b], T. Hofmann [e,b], M. Schubert [e,b], T.E. Tiwald [f], M. Solinsky [g], M. Wagner [g]

[a] Department of Chemical and Biomolecular Engineering, University of Nebraska-Lincoln, USA
[b] Nebraska Center for Materials and Nanoscience, University of Nebraska-Lincoln, USA
[c] Department of Biological Systems Engineering, University of Nebraska-Lincoln, USA
[d] Biomedical Engineering Program, University of Nebraska-Lincoln, USA
[e] Department of Electrical Engineering, University of Nebraska-Lincoln, USA
[f] J.A. Woollam Co., Inc., 645 Main Street, Suite 102, Lincoln, NE 68508, USA
[g] The Procter & Gamble Company, 11810 E. Miami River Rd., Cincinnati, OH 45252, USA

ARTICLE INFO

Available online 13 December 2010

Keywords:
Spectroscopic ellipsometry
Quartz crystal microbalance
Self-assembled monolayers
SAMs
Alkanethiols

ABSTRACT

Self-assembled monolayers (SAMs) formed via chemisorption are important for a variety of surface enhancement and biological applications. We demonstrate that combinatorial spectroscopic ellipsometry (SE) and quartz crystal microbalance with dissipation (QCM-D) provides dynamic, *in-situ* characterization of the chemisorption process. In agreement with other studies, we find there are two steps for 1-decanethiol, an example alkanethiol SAM, chemisorption onto gold, which are a brief, fast phase followed by one that is long but slower. By using both the optical (SE) and mechanical (QCM-D) techniques, we show that the SAM porosity decreases during the second phase as the coupled ethanol solvent in the disorganized layer is replaced by more alkanethiol.

1. Introduction

Self-assembled monolayers (SAMs) of alkanethiols on gold create surfaces with a high degree of molecular order and packing. The methods for the preparation, analysis, and applications are believed to be well understood, including assembly mechanisms and kinetics. Alkanethiols consist of a carbon chain, a thiol group on one end (head group) that has a high affinity for the gold substrate, and a predetermined functional group at the tail end that interacts with the environment. Most studies concur that alkanethiols are densely packed into a hexagonal lattice conformation, with the alkanethiols having a tilt angle of approximately 30° from the surface normal [1,2]. However, knowledge on the actual conformation of the molecules is not exhaustive.

SAMs are inexpensive, can coat non-uniform surfaces, and have a variety of applications as surface modifiers to regulate wetting and charge, purify water, protect materials from corrosion, and enhance the subsequent attachment of certain molecules [3–5]. SAMs have the ability to be used as model biomaterials to investigate surface property effects on protein adsorption and cellular adhesion and responses [3].

We elect to study SAMs from the standpoint of simultaneous optical and mechanical *in-situ* instrumentation for two reasons. With spectroscopic ellipsometry (SE, optical) and quartz crystal microbalance with dissipation (QCM-D, mechanical) techniques, one can determine the porosity, an important indicator of molecular configuration, of organic ultra-thin films. Second, SAMs are important for more complex systems where a SAM yields important surface properties; for example, proteins and cells could be adsorbed onto a SAM providing favorable surface chemistry. Such systems are of interest for future study.

SE is a non-contact, non-destructive optical technique that allows one to acquire the indices of refraction, $n(\lambda)$; extinction coefficients, $k(\lambda)$; and thicknesses, d; of uniformly parallel layers [6,7]. However, for ultra-thin transparent films (i.e., with thickness much less than the probing wavelength), the index-thickness product cannot be separated, and either n or d must be assumed. A QCM-D measures shifts in frequency, $\delta\nu_N$, and dissipation, δD_N, of vibrational resonance overtones to determine the mass coupled to a coated quartz crystal sensor and to what degree the film is viscoelastic [8].

SAMs are widely investigated with non-combinatorial SE approaches. Prato et al. studied thiolate polydiacetylene (PDA) SAMs with *ex-situ* SE complemented with X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) to observe exciton absorptions in the PDA SAMs, examine polymerization of PDA SAMs, and investigate the interaction between adsorbent and

---

* Corresponding author. Department of Chemical and Biomolecular Engineering, University of Nebraska-Lincoln, USA.

E-mail addresses: kbrod@cox.net (K.B. Rodenhausen), schubert@engr.unl.edu (M. Schubert).

0040-6090/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2010.11.081

substrate [9]. They found that SE was sensitive to SAM absorption in the UV–vis range and PDA SAM polymerization predominately occurred on locally smooth regions with roughness less than 1 nm.

SE and QCM-D each give independent information that is needed when considering organic thin film conformation. SE detects only the organic adsorbent attached to the quartz sensor while the QCM-D is sensitive to the combined adsorbent and coupled solvent mass. We direct the reader interested in technical details of our combinatorial SE/QCM-D approach to other contributions in these proceedings [10,11].

In this work, we present preliminary results of alkanethiol SAM chemisorption onto gold as studied by our hybrid experimental setup and discuss them in the context of previous investigations.

2. Theory

Consider the scenario of a multilayer sample with parallel, uniform interfaces. For transparent organic ultra-thin films that meet the criterion $2\pi nd/\lambda \ll 1$, where $\lambda = 2\pi c/\omega$ is the wavelength of the probing light, SE is not sensitive to layer order; it is possible to arbitrarily change the layer order or to segregate a heterogeneous film into one that has a set of perfectly homogenous layers [10]. One can then rearrange a porous film such that all associated solvent is moved to the top. It follows that an ambient-ambient interface is formed that does not affect the system.

Thus, we find that the ultra-thin film thickness detected by SE (d_{SE}) excludes solvent. d_{SE} is obtained by applying an optical model (substrate-single layer-ambient) and fitting for the adsorbent layer thickness while assuming the indices of refraction of the segregated organic layer, $n_{\mathrm{o}}(\lambda)$, with the CompleteEASE (J.A. Woollam Co., Inc.) software program.

QCM-D measures frequency and dissipation shifts of odd harmonic resonance overtones through the program, QSoft (Biolin Scientific), and these shifts are generally related to bulk property and adsorbent mass changes and viscoelasticity changes, respectively [8]. The QCM-D data showed that the maximum dissipation shift (omitted for brevity) during the measurements was small relative to the frequency shifts, so the film was assumed to be rigid and thus follow the Sauerbrey relation [12],

$$\delta\Gamma_{\mathrm{QCM}} = \mathrm{C}\frac{\delta\nu_{\mathrm{N}}}{\mathrm{N}}, \tag{1}$$

where $\delta\nu_{\mathrm{N}}$ is the frequency shift of the frequency overtone N and constant C is 17.7 ng/(cm^2 Hz). In this manner, QCM-D determines the change in surface mass density $\delta\Gamma_{\mathrm{QCM}}$ of the adsorbent plus any associated solvent. $\delta\Gamma_{\mathrm{QCM}}$ converts to d_{QCM}, the film thickness that also accounts for coupled solvent, via the total attached physical layer density, which is mathematically described as an “effective” density, ρ_{eff}.

One can refer to porosity as a volume or mass fraction parameter. Such a parameter is set up as a simple ratio of ambient content (V_{a} or m_{a}) to total “effective” sum (V_{eff} or m_{eff}) to yield

$$f_{\mathrm{a}}^{\mathrm{V}} = \frac{V_{\mathrm{a}}}{V_{\mathrm{eff}}} = \frac{V_{\mathrm{a}}}{V_{\mathrm{o}} + V_{\mathrm{a}}}, \tag{2}$$

$$f_{\mathrm{a}}^{\mathrm{m}} = \frac{m_{\mathrm{a}}}{m_{\mathrm{eff}}} = \frac{m_{\mathrm{a}}}{m_{\mathrm{o}} + m_{\mathrm{a}}}. \tag{3}$$

The basis for obtaining the fraction parameters stems from the relationship between the SE and QCM-D measured data, X^{SE} and X^{QCM}, respectively,

$$f_{\mathrm{o}}^{\mathrm{m}} = 1 - f_{\mathrm{a}}^{\mathrm{m}} = \frac{m_{\mathrm{o}}}{m_{\mathrm{o}} + m_{\mathrm{a}}} = \frac{\rho_{\mathrm{o}}}{n_{\mathrm{o}}}\frac{X^{\mathrm{SE}}}{X^{\mathrm{QCM}}}, \tag{4}$$

where we define

$$X^{\mathrm{SE}} = d_{\mathrm{o}} n_{\mathrm{o}} = d_{\mathrm{SE}} n_{\mathrm{o}}, \tag{5}$$

$$X^{\mathrm{QCM}} = d_{\mathrm{eff}}\,\rho_{\mathrm{eff}} = d_{\mathrm{QCM}}\,\rho_{\mathrm{eff}}. \tag{6}$$

In our virtual separation approach, we usually assume n_{o} and ρ_{o} while also using easily found ρ_{a} [10]. For completion, an expression for $f_{\mathrm{o}}^{\mathrm{V}}$ must be obtained in terms of known, assumed, or experimentally determined quantities, as in the case of Eq. (4). The volumes of Eq. (2) can be written out as thickness-area products such that

$$f_{\mathrm{a}}^{\mathrm{V}} = \frac{d_{\mathrm{a}}A}{d_{\mathrm{eff}}A} = \frac{d_{\mathrm{a}}}{d_{\mathrm{eff}}} = \frac{d_{\mathrm{QCM}} - d_{\mathrm{SE}}}{d_{\mathrm{QCM}}}. \tag{7}$$

Similarly, for Eq. (3) it follows that

$$f_{\mathrm{a}}^{\mathrm{m}} = \frac{\rho_{\mathrm{a}} d_{\mathrm{a}}}{\rho_{\mathrm{a}} d_{\mathrm{a}} + \rho_{\mathrm{o}} d_{\mathrm{o}}} = \frac{\rho_{\mathrm{a}}(d_{\mathrm{QCM}} - d_{\mathrm{SE}})}{\rho_{\mathrm{a}}(d_{\mathrm{QCM}} - d_{\mathrm{SE}}) + \rho_{\mathrm{o}} d_{\mathrm{SE}}}. \tag{8}$$

It can thus be explicitly shown that if $\rho_{\mathrm{a}} = \rho_{\mathrm{o}}$, the right side of Eq. (8) reduces to that of Eq. (7), so $f_{\mathrm{a}}^{\mathrm{V}} = f_{\mathrm{a}}^{\mathrm{m}}$. If the constituent densities are not equal, the effective density is

$$\rho_{\mathrm{eff}} = \frac{m_{\mathrm{eff}}}{V_{\mathrm{eff}}} = \frac{m_{\mathrm{a}}}{V_{\mathrm{eff}}} + \frac{m_{\mathrm{o}}}{V_{\mathrm{eff}}} = \rho_{\mathrm{a}} f_{\mathrm{a}}^{\mathrm{V}} + \rho_{\mathrm{o}}\left(1 - f_{\mathrm{a}}^{\mathrm{V}}\right), \tag{9}$$

meaning the relationship between $f_{\mathrm{a}}^{\mathrm{V}}$ and $f_{\mathrm{a}}^{\mathrm{m}}$ can be written as

$$f_{\mathrm{a}}^{\mathrm{V}} = f_{\mathrm{a}}^{\mathrm{m}}\frac{\rho_{\mathrm{eff}}}{\rho_{\mathrm{a}}} = \frac{\rho_{\mathrm{o}}}{\rho_{\mathrm{a}}}\frac{f_{\mathrm{a}}^{\mathrm{m}}}{\left(1 - f_{\mathrm{a}}^{\mathrm{m}} + f_{\mathrm{a}}^{\mathrm{m}}\frac{\rho_{\mathrm{o}}}{\rho_{\mathrm{a}}}\right)}. \tag{10}$$

The adsorbent volume fraction, $f_{\mathrm{o}}^{\mathrm{V}}$ is $1 - f_{\mathrm{a}}^{\mathrm{V}}$.

3. Experiment

The alkanethiol (1-decanethiol) for the experiments was purchased from Sigma-Aldrich. 2 mM alkanethiol solution was made with 200 proof ethanol purchased from Pharmco that was degassed and filtered before preparation. No other additives were included. The substrate was an AT cut quartz crystal coated with a 100 nm layer of gold. The sensors were manufactured by Q-Sense and used without modification. The QCM-D sensors had a resonance frequency 4.95 MHz ± 50 kHz, and the root mean square surface roughness of the gold layer was less than 3 nm. The gold layer was optically opaque for the subsequent SE study.

The experimental setup and pre-measurement protocols are discussed in detail elsewhere [10,11]. In summary, the setup consists of an M-2000-V SE (J. A. Woollam Co., Inc.) that measures 512 wavelengths in the visible-near UV spectrum simultaneously and an E1 QCM-D (Biolin Scientific). For this study, we assumed $n_{\mathrm{o}} = 1.5$, independent of wavelength. At the controlled temperature of 19 °C, the density of ethanol (ρ_{a}) is 0.790 g/mL. Because 1-decanethiol is a liquid at room temperature, a referenced ρ_{o} is not prone to complications such as molecular packing. Sigma-Aldrich gives the density of 1-decanethiol used in the experiment as 0.824 g/mL. Thus, $f_{\mathrm{o}}^{\mathrm{V}}$ and $f_{\mathrm{o}}^{\mathrm{m}}$ are not equivalent.

The alkanethiol feed solution was pumped through the liquid cell at a rate of 0.4 mL/min for approximately 30 min by a programmable syringe pump manufactured by New Era Pump Systems, Inc. Then the solution within the liquid cell remained stagnant overnight.