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The retention of liquid by columnar nanostructured surfaces during quartz crystal microbalance measurements and the effects of adsorption thereon

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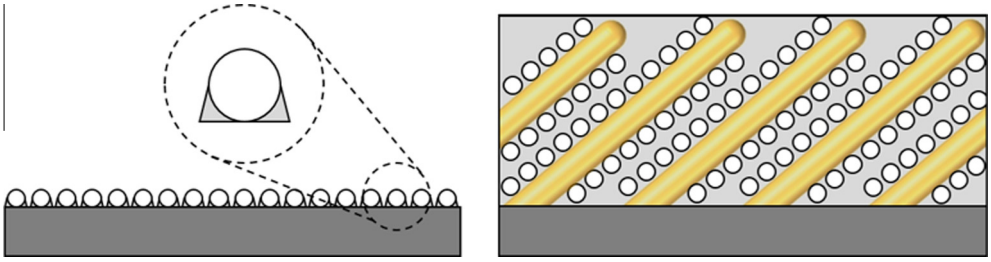
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: A surface comprising spatially coherent columnar nanostructures is expected to retain intercolumnar liquid during a quartz crystal microbalance measurement due to the surface structure. Part of the liquid retained by the nanostructures may then be displaced by adsorbate.

Experiments: Slanted columnar nanostructure thin films were designed to vary in height but remain structurally similar, fabricated by glancing angle deposition, and characterized by generalized ellipsometry. A frequency overtone analysis, introduced here, was applied to analyze quartz crystal microbalance data for the exchange of isotope liquids over the nanostructured surfaces and determine the areal inertial mass of structure-retained liquid. The adsorption of cetyltrimethylammonium bromide onto nanostructures was investigated by simultaneous quartz crystal microbalance and generalized ellipsometry measurements.

Findings: The areal inertial mass of structure-retained liquid varies linearly with nanostructure height. The proportionality constant is a function of the surface topography and agrees with the generalized ellipsometry-determined nanostructure film porosity, implying that nearly all intercolumnar liquid is retained. We report that for adsorption processes within porous nanostructured films, the quartz crystal microbalance is sensitive not to the combined areal inertial mass of adsorbate and retained liquid but rather to the density difference between adsorbate and liquid due to the volume exchange within the nanostructure film.

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1. Introduction

Adsorption and desorption processes [1–3], surface chemical reactions [4,5], and reorganization of chemical species [6,7] and the kinetics thereof are widely studied at the solid–liquid interface. Thus far, such processes are commonly studied on flat surfaces. The quartz crystal microbalance (QCM) technique is used to monitor these processes and allows for the determination of the areal inertial mass (i.e., surface inertial mass density) of an adsorbate layer. In addition to adsorbate, the layer may comprise liquid that hydrates, for example, and is retained by the adsorbate. It is well-known that QCM measurements do not permit the differentiation between the areal inertial mass of adsorbate and the retained liquid on flat surfaces, and it is often reported that QCM data analysis "overestimates" the areal inertial mass of adsorbate [1,6,8–10]. Optical techniques such as ellipsometry [7,8,11–13], reflectometry [14,15], surface plasmon resonance spectroscopy [16,17], and dual-polarization interferometry [18,19] have also been used to monitor adsorption of organic molecules independently of or in conjunction with QCM or a further development of QCM known as quartz crystal microbalance with dissipation (QCM-D). The use of an optical technique in tandem with QCM or QCM-D may allow for the determination of the adsorbate layer porosity [20–22].

Three-dimensional (3D) spatially coherent nanostructured films, such as slanted columnar thin films (SCTFs) produced by glancing angle deposition (GLAD) [23,24], are emerging as scaffolding materials upon which adsorption processes may be evaluated [25–28]. SCTFs have many advantages over flat surfaces; SCTFs have increased surface area, have spatial dimensions that may be controlled by their fabrication process [23,24,29], may act as molecular filters or storage [27,28], have strongly anisotropic optical properties for sensor applications [26,30,31], provide improved biocompatibility with cells due to their topography [25,28], and may be fabricated from materials that result in films exhibiting the surface-enhanced Raman scattering (SERS) effect [32].

It is hypothesized here that liquid within a SCTF may be retained in the absence of adsorbate by the oscillating nanostructures during a QCM measurement. Thus, adsorbate that attaches within a SCTF during a QCM measurement may not retain further liquid and may liberate displaced liquid that was formerly retained. The different mechanisms of liquid retention between flat and SCTF surfaces may provide an avenue for QCM to differentiate between adsorbate and retained liquid without the need for additional techniques.

Martin et al. used flat and rough surfaces to simultaneously determine the density and viscosity of liquids by QCM, alone [33]. The difference between flat and SCTF surfaces on the amount of liquid retained during a QCM measurement in the presence of adsorbate is illustrated by Fig. 1. The purpose of this work is to determine whether all, part, or none of the liquid within a SCTF is retained during QCM measurement. Additionally, it must be determined whether an adsorption process into a SCTF has an additive, neutral, or deleterious effect on the areal inertial mass of retained liquid.

QCM is a mechanical technique whereby a piezoelectric AT-cut quartz crystal sensor oscillates in a shear mode at its resonance frequency under an applied alternating potential. Variations of the areal inertial mass and variations of the bulk liquid density and viscosity modulate the frequency of oscillation ν. Existing approaches to model the effects of liquid properties on the QCM response become unsuitable as random surface roughness increases [34]. SCTFs, however, are "super-rough" surfaces and thus require the advancement of existing data analysis approaches, which may allow for the determination of areal inertial mass of retained liquid in highly ordered 3D nanostructure thin films.

The use of deuterated liquids to determine the porosity and areal inertial mass of an adsorbate layer on a flat surface with QCM, alone, was introduced by Craig and Plunkett [35]. This method requires the surface to be measured under a liquid and the liquid's deuterated analog before and after adsorbate layer formation. The deuterated liquid is assumed to be chemically identical to non-deuterated liquid and has a larger density. If the QCM chamber ambient is changed from air to liquid, the QCM-measured frequency shift is ideally larger for the deuterated liquid than the non-deuterated liquid. However, the processes of filling the QCM chamber with liquid or emptying liquid out of the chamber may cause irreproducible frequency shifts due to pressure changes. Instead, the deuterated and non-deuterated liquids may be cycled through the QCM chamber to more closely maintain isobaric conditions. One thus measures the two frequency shifts between (a) the bare surface exposed to deuterated and non-deuterated liquids and (b) the surface with adsorbate exposed to deuterated and non-deuterated liquids (alternatively a bare surface exposed to deuterated and non-deuterated liquids with dissolved adsorbate). These measurements allow for determination of the fraction of the frequency shift between the bare surface and the surface with adsorbate under non-deuterated liquid that is due to retained liquid rather than adsorbate [35]. This strategy has been used to quantify the areal inertial mass and porosity of organic layers, including polyelectrolyte multilayers [36] and polysaccharides [37–39]. Due to its highly ordered geometry and porous structure, a mechanically oscillating SCTF interacts with the bulk liquid differently than a flat surface, and so the method of Craig and Plunkett may not be readily applicable. Additional theoretical work is required for the analysis of QCM data for highly ordered 3D surfaces. Specifically, the capability to quantify retained liquid, which may be described by a porosity parameter intrinsic to the SCTF geometry, is desired.

Generalized ellipsometry (GE) is an optical technique that measures the change of the polarization state of light after it reflects off of or transmits through a sample, particularly anisotropic materials such as SCTFs [40,41]. GE measures elements of the 4×4 Mueller

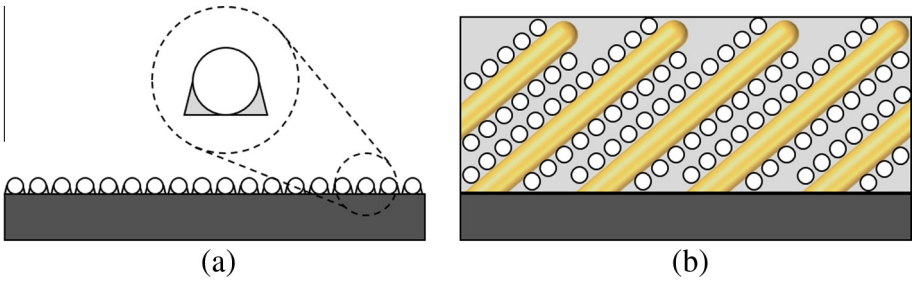

Fig. 1. (a) Adsorbate (here depicted by particles) attached to a flat surface. During QCM measurement, each particle retains liquid (shaded). In this case the retained liquid may be arranged, for example, in a conal distribution. Alone, QCM is generally not sensitive to the distribution of retained liquid or to the areal inertial mass ratio of adsorbate to retained liquid. (b) Adsorbate particles attached to a SCTF. During QCM measurement, liquid is retained by the nanostructured surface. Liquid retention by the SCTF implies that adsorbate displaces retained liquid and hence partially offsets the measured frequency shift.