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Measuring the Surface Roughness of Sputtered Coatings by Microgravimetry

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A novel application of quartz crystal microgravimetry is described to enable determination of the roughness of native and sputtered oxide coatings. The technique is applicable to coatings that may be too rough for accurate atomic force microscopic imaging where measurements may be limited by the dimensions of the probe tip.

Interfacing organics with solids impacts myriad fields of materials science, ranging from implant materials,[1] to chemical sensors,[2] to microelectronic devices,[3] to name a few. Successful interface synthesis relies on careful application of surface organic chemistry in order to achieve uniform film growth of target organics on a chosen substrate. In this context, the microscopic surface area of the substrate is an important parameter in the evaluation of film structure, density, and surface reaction yield, yet surface area can be an ill-defined property because of the relative length scale of measurement for this parameter and the roughness of the surface: An optically flat surface can have its geometric surface area calculated from its macroscopic dimensions, but its microscopic surface area could be far greater due to surface convolutions that are not optically detectable. The ratio of the microscopic surface area to the geometric surface area is a measure of surface roughness, the "roughness factor," incorporating the size and spatial distribution of irregularities on a surface. In principle, measuring roughness with a probe of similar or smaller dimension to these surface features can lead to a more accurate surface area measurement.

Atomic force microscopy (AFM) is a popular method of choice in materials science and surface chemistry to evaluate surface morphology and to obtain a measure of surface roughness. However, AFM has limitations: Some surfaces, such as sputtered oxides, can be too convoluted to image accurately by AFM if the tip profile dimensions are large compared to surface features;[4] indeed, surface roughness determinations from AFM data might underestimate surface area by as much as 20%.[5] Roughness measured by AFM is also characteristic only of the relatively small area imaged by the probe microscope, so surface heterogeneities could seriously affect the overall microscopic roughness of the samples as determined by AFM. An independent check on AFM roughness determinations on the molecular scale for sputtered substrates of interest to us was thus necessary. We now demonstrate that a simple adaptation of quartz crystal microgravimetry can be used to measure the roughness of such surfaces.

The benchmark technique for using a molecular probe to directly measure surface area (per unit weight) of high-surface-area materials is the Brunauer−Emmet−Teller (BET) method,[6] which is based on the adsorption of a probe molecule onto a surface. The BET isotherm[7] (eq 1) relates χ, the relative pressure (p/p_0) of the probe molecule, n, the total mass of adsorbed probe molecule, and n_m, the mass of the probe molecule that forms a monolayer over the substrate; C is a dimensionless constant (eq 1).

$$\frac{\chi}{n(1-\chi)} = \frac{1}{n_m C} - \frac{(C-1)}{n_m \chi} \tag{1}$$

Typical BET procedures quantify probe molecules adsorbed on a substrate surface directly, usually volumetrically. This amount is then related to the substrate surface area by assuming a particular cross sectional area for the adsorbed probe molecule. While the BET method does not suffer from the probe size limitation of scanning probe microscopies, it does require a sizable quantity (usually microgram) of a high-surface-area substrate to ensure that probe molecule loadings are accurately measured. However, the need for these large quantities of adsorbate can be obviated by using quartz crystal microgravimetry to determine the amount of probe molecule adsorbed. A typical quartz crystal microbalance (QCM) is capable of measuring mass loadings on a surface of less than 1 ng/cm^2.[8] This mass loading is determined according to eq 2,[9] where the decrease in the fundamental frequency (Δf) of a crystal vibrating in shear mode is proportional to the change in mass (Δm) introduced onto the surface of that crystal (C_f is a constant). The relationship between an observed frequency change of a QCM and the partial pressure of an adsorbate above the electrode surface can thus be determined (eq 3), and the frequency change at *monolayer* coverage (Δf_m) of the adsorbate can then be calculated from the slope and intercept of the BET isotherm ($1/\chi$ vs $\chi/[\Delta f\,(1-\chi)]$).

$$\Delta f = -C_f\,\Delta m \tag{2}$$

$$\frac{\chi}{\Delta f(1-\chi)} = \frac{1}{\Delta f_m C} - \frac{(C-1)}{\chi \Delta f_m} \tag{3}$$

The frequency change at monolayer coverage can then be used to calculate the area covered by the monolayer if the cross-sectional area of the probe molecule is known.

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Lando and Slutsky first used the QCM−BET method to measure the mass of adsorbate molecules on a gold-coated QCM electrode as a function of the adsorbate pressure.[10] Using cross-sectional areas derived from the bulk density of various adsorbates, they then estimated the surface roughness of the sputtered gold. Since the goal of their work was to determine the potential of interaction between the adsorbate molecules and the gold substrate, some idea of surface roughness was necessary to provide an incidental correction to their estimated surface area, which in turn was needed for evaluation of the interaction potential; however, they did not apply this approach to an independent determination of surface roughness for other substrates.

The advent of AFM as a means to measure surface roughness is based on the assumption that the probe tip faithfully traces the peaks and valleys of even highly convoluted surfaces. The validity of this assumption, however, must be called into question where the aspect ratio of features of rough surfaces are sufficiently large that such tracing is precluded. As a check on the accuracy of the AFM method to analyze rough surfaces, we developed a modified BET−QCM method to study oxide-coated materials of high microscopic roughness. We found that good, quantitative correspondence exists between the AFM and BET−QCM techniques for surfaces of low roughness but that, as we reasoned, the AFM method underestimated surface areas for a highly rough oxide.

Experimental

Tetramethylsilane (TMS; Aldrich, 99.99+%) was used as received. QCMs used were AT-cut, 10 MHz, overtone polished crystals equipped with gold electrodes (0.201 in. diam; International Crystal Manufacturing, ICM). These electrodes were then coated with Ti, Si, or indium tin oxide (ITO; 1000 Å thick); all surfaces were optically flat. An ICM oscillator (Model 35360) was used to drive the crystals, and the resonant frequency of each was monitored using a Hewlett-Packard 5200 series frequency counter. Each microbalance was rinsed first under a stream of methanol and then with distilled water (Milli-Q). They were then mounted in an evacuable chamber fitted with electrical feed-throughs. The chamber was evacuated to <1 Torr and was kept under active vacuum until the resonant frequency stabilized (typically 30 min), indicating that rinsing solvent had evaporated. The chamber was then isolated from the vacuum pump and was opened to a reservoir containing the TMS, which was immersed in a water bath. The chamber was filled with TMS to its full vapor pressure, as determined by an Hg manometer. The vapor pressure of TMS was recorded, and the chamber was re-evacuated. This procedure was repeated three times. QCM frequency change data are shown in Figure 1 for a typical experimental run; these data show the stability of our system used to obtain the isotherms for TMS adsorption. To verify that the adsorption of TMS was reversible, the resonant frequency of the crystal was monitored each time the chamber was evacuated. An adsorption isotherm for each surface was obtained by monitoring the frequency response of the crystal from <1 to 630 Torr in 10 Torr increments.

Results and Discussion

The resonant frequency of a QCM crystal is affected not only by electrode mass changes by molecular adsorption but also by the presence of the adsorbate species vapor; hydrostatic pressure affects the shear moduli of quartz, and the adsorbate vapor produces aerodynamic drag. Hydrostatic effects are small and are not a serious source of error.[11] To determine the magnitude of the aerodynamic drag, the frequency response of a QCM crystal to pressure change between 30 and 300 Torr was probed using dry nitrogen at room temperature. The crystal frequency response to this change in pressure in the range of interest for our surface area measurements was negligible.

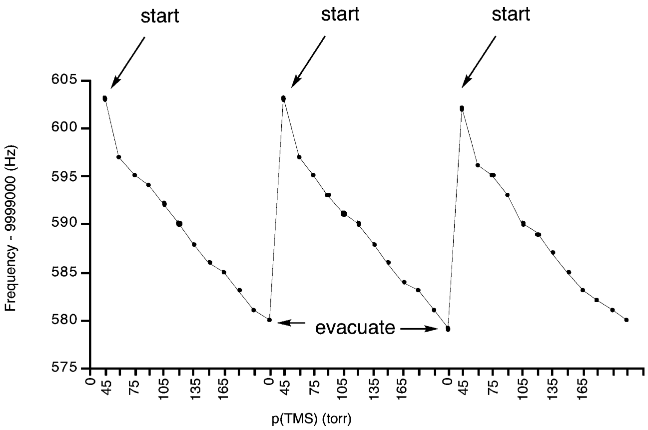

Figure 1. Three successive QCM runs for measuring surface roughness of the native oxide coating on Si showing the oscillator frequency (Hz) during TMS adsorption and following re-evacuation.

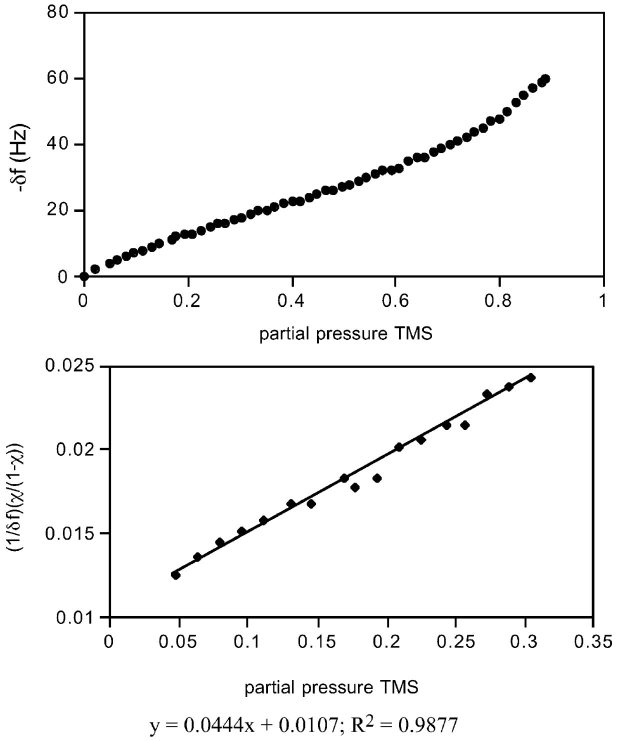

Figure 2. TMS adsorption isotherm on gold.

AT-cut crystals have only a small window of thermal stability centered near 20 °C,[12] so TMS was chosen as our probe molecule: TMS is nonpolar, relatively spherical, and nonreacting, with a boiling point near room temperature. TMS adsorption isotherms on gold, native oxide-coated Si, and indium tin oxide are shown in Figures 2−4; each has a sigmoidal shape and is consistent with a Type II isotherm,[13] which results from reversible monolayer physisorption of adsorbate molecules on nonporous substrates and is interpretable according to the BET method. Under these conditions, TMS is most likely to form a single physisorbed monolayer on a range of surfaces, with little

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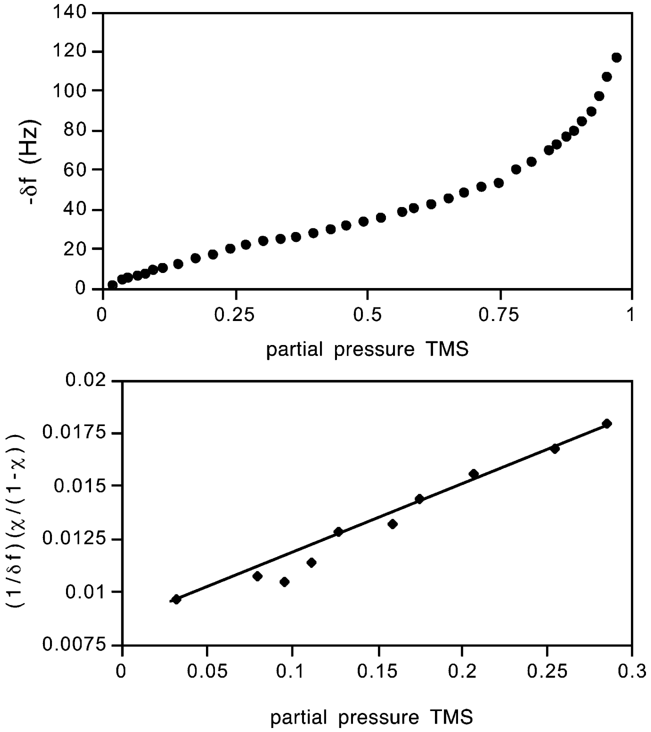

Figure 3. TMS adsorption isotherm on silicon.

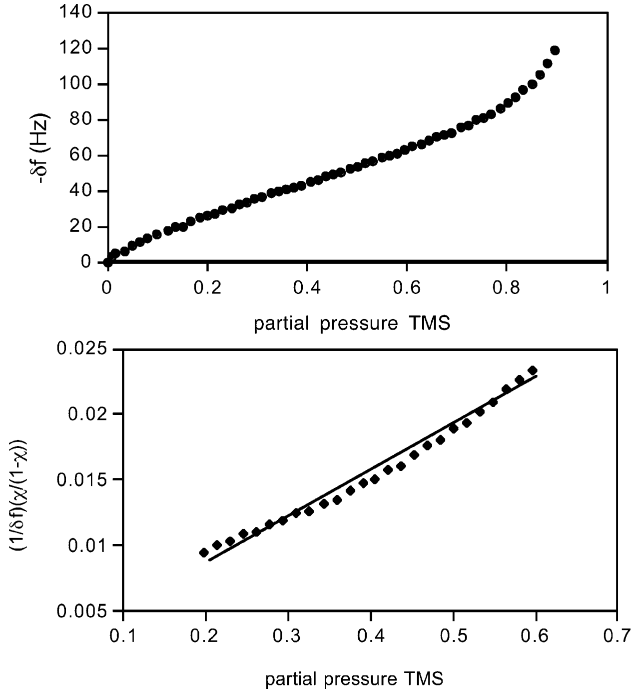

Figure 4. TMS adsorption isotherm on indium tin oxide (ITO).

variation in monolayer packing density, regardless of substrate. The method described herein is based on this assumption, which would break down for substrate temperatures far lower or higher than the boiling point of TMS or for highly porous substrates.

The cross-sectional area of TMS was calculated using a sputtered gold electrode; such gold films are known to be optically flat, crystalline, and smooth.[14] AFM analysis of the Au film was used to calculate a roughness factor of 1.1 for this surface. QCM−BET measurements on Au using this factor were then used to measure the TMS molecular cross-sectional area, which was found to be 37.6 Å^2, comparing favorably with that value (40.4 Å^2) calculated from the bulk density of TMS[10] (Figure 5).

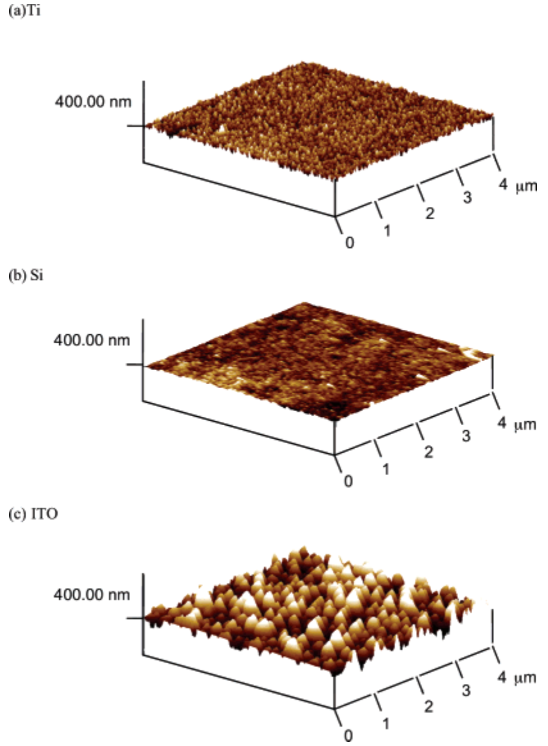

Figure 5. AFM images for (a) the native oxide coating on Ti; (b) the native oxide coating on Si and (c) ITO.

Table 1. Summary of Coating Roughness (*R*)

parameter	Au	Ti	Si	ITO
δf_m (Hz)	18.18	20.31 ± 2.6	21.8 ± 1.1	27.1 ± 1.4
δm (μg)	0.0164	0.0184	0.0196	0.02454
area (cm^2)	0.449	0.501 ± 0.065	0.534 ± 0.027	0.670 ± 0.035
R_{BET}	–[a]	1.22 ± 0.16	1.31 ± 0.07	1.63 ± 0.09
R_{AFM}	1.10	1.20	1.21	1.45
deviation (%)[b]	–	1.7	8.3	12.4

[a] The standard surface; R_{BET} set at 1.10 to determine the cross-sectional area of TMS. [b] Deviation measured as the ratio of R_{BET}/R_{AFM}.

Using the QCM−BET method, microscopic surface areas of sputtered Ti, Si, and ITO were measured; roughness values for these surfaces were determined (Table 1) and compared with calculations based on AFM measurements. As can be seen from the data in Table 1, the agreement between roughness determined by the QCM−BET method and that based on AFM measurements is quite good for the Au and the oxidized Ti or Si surfaces. The ITO surface, which is quite rough and not well-imaged by AFM,[15] was easily probed by QCM−BET. For this surface, the QCM−BET method gave a roughness factor of 1.6; the isotherm for ITO was completely reversible, indicating that this surface is not mesoporous and that this value is an accurate measure of overall surface roughness.

Conclusions

We have described a convenient method for measuring the roughness of thin films using the BET method combined with quartz crystal microgravimetry. This approach provides roughness measures that are in good

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agreement with those determined by AFM for surfaces of low to moderate roughness. Significantly, the QCM−BET method can also be used to determine roughness of high-aspect-ratio, nonporous films that cannot be adequately imaged by AFM, such as the sputtered ITO film described herein. Furthermore, the QCM−BET method gives an overall roughness determination that is not limited to the small areas typically imaged by scanning probe microscopies.

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