Supplemental Information

"Thin silica films on Ru(0001): Monolayer, bilayer and three-dimensional networks of $[SiO_4]$ tetrahedra"

by

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Thickness determination via XPS.

To provide a means of directly ascertaining film thicknesses from XPS intensities (i.e., without necessitating direct comparison with $SiO_{2.5}$/Mo(112) samples), we provide a series of XPS measurements in Fig. S1, which are representative of films corresponding to ~0.5, 1, and 2 MLE Si. For these experiments, we have used identical analyzer conditions, with a fixed pass energy of 20 eV, to obtain all spectra provided. As can be seen, mono- and sub-monolayer films show Si 2p and O1s peak shifts of ~0.2-0.3 eV to lower binding energies relative the values observed for bilayer films (Fig. S1-a). When integrating the peak intensities, we note roughly linear growth (attenuation) of the Si and O (Ru) peaks as a function of Si exposure. As such, we have made use of the linear trendlines shown to back out the following XPS-based thickness estimating equations:

(1) $$\frac{Ru{:}Ru_0-1}{-0.143} = x\ MLE\ Si$$

(2) $$\frac{Si{:}Ru}{0.010} = x\ MLE\ Si$$

(3) $$\frac{O{:}Ru-0.003}{0.120} = x\ MLE\ Si$$

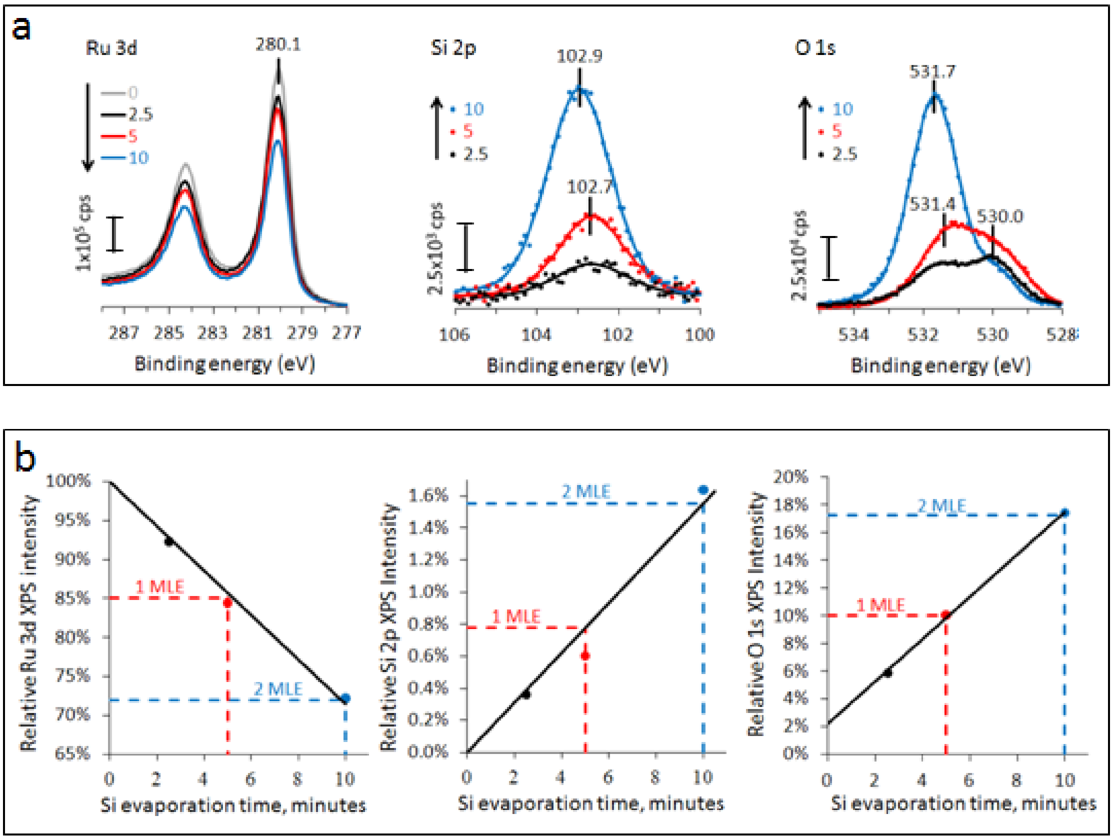

Figure S1. (a) XPS spectra of the Ru 3d (left), Si 2p (middle), and O 1s peaks (right) for films created via 0 (grey), 2.5 (black), 5 (red), and 10 minute (blue) exposures to the Si evaporator. (b) Quantitative analysis of the peaks shown in (a) as a function of evaporator exposure time, with all intensities plotted relative to the intensity of clean Ru.

where Ru, Si, O are the Ru 3d, Si 2p, and O 1s peak intensities recorded for a given film with a thickness of x MLE Si. Ru_0 is then the Ru 3d peak intensity recorded for clean Ru.

Growth mode vs. thickness via ISS

Figure S2 shows ISS data collected from the samples used to create the thickness dependent XPS plots in Fig. S1. As can be seen in Fig. S2-a, the ISS peak assigned to surface-bound O is roughly unaffected by variation in the Si exposure used during film preparation. This is consistent with our models for both monolayer and bilayer film growth, which both show

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concentrations of terminally bound O that are equivalent to the concentration of O found within our 3O(2x2)-Ru precursor state. As such, the ISS peak intensity is expected to remain

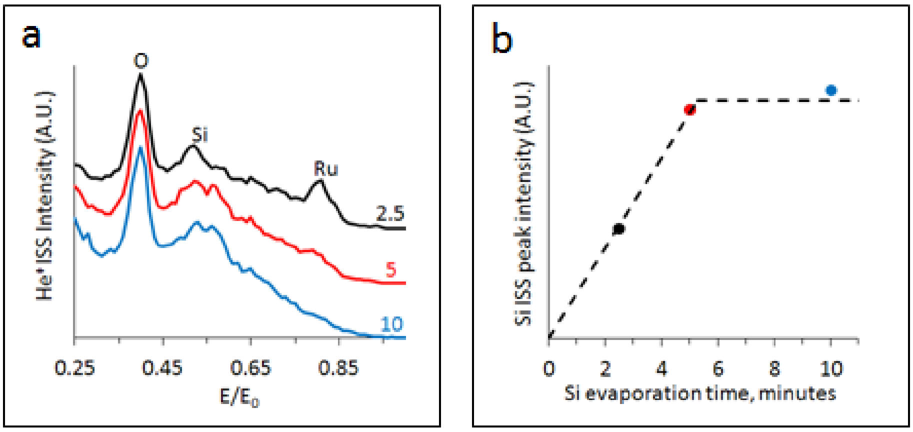

Figure S2. (a) ISS spectra from films created 2.5 (black), 5 (red), and 10 minute (blue) exposures to the Si evaporator. (b) Quantitative analysis of the Si peaks shown in (a), plotted as a function of evaporator exposure time.

constant throughout the film growth since any open patches in the film will reveal the same number of Ru-bound O's as are present in the termination of either film, and any signal expected from chemisorbed O that may be present below the film will go undetected due to blocking and shadowing effects of the overlayer film.

In contrast to the O peak, both the Ru and Si features show variation in peak intensity as a function of Si exposure during film growth. As can be seen, the Ru peak is attenuated, and the Si peak increases, with increasing Si exposure. Both effects are expected as the film covers an increasing percentage of the surface. Most of this change occurs between the samples prepared via 2.5 and 5 minutes of Si exposure, and only little change is noted in the size of the peaks when further increasing the dose to 10 minutes. This trend is shown quantitatively for the Si peak in Fig. S2-b. Consistent with our "monolayer precedes bilayer" growth mechanism, the peak intensity saturates at the point where XPS suggests we have the monolayer film described in Fig.'s 2 and 3 of the main text. Little change is noted beyond this exposure because the bilayer termination is identical to that of the monolayer.