Advances in surface plasmon resonance imaging enable quantitative tracking of nanoscale changes in thickness and roughness

Supplemental Information

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S1. SPR Curves for Bare Gold Film and PMMA Film on Gold Film

SPRi measurements were performed on multiple regions of a patterned PMMA film on a gold film on a high index ($n = 1.71126$ at $\lambda = 794.7$ nm) glass slide in water. In one representative region of interest (ROI), the PMMA film was uniformly removed by e-beam patterning (“bare gold” film). In a second ROI, the PMMA film is of uniform thickness. Representative SPR curves measured on these ROIs and the corresponding best-fit SPR curves are shown in Figures S1 (bare gold film) and S2 (PMMA film on gold film).

Figure S1: A representative experimental SPR curve of reflectivity versus angle of incidence $\theta_i$ for a ROI tracked in many SPR images of a uniformly exposed PMMA film (“bare gold” film) immersed in water (black points) and the SPR curve calculated using the best-fit values of $n_{Au} = 0.1509 + 5.0755i$, $h_{Au} = 38.1$ nm, $n_{water} = 1.3332$ (red curve).
Figure S2: A representative experimental SPR curve of reflectivity versus angle of incidence $\theta_i$ for a ROI tracked in many SPR images of a PMMA film of uniform thickness (black points) and the SPR curve calculated using the best-fit values of $n_{Au} = 0.1509 + 5.0755i$, $h_{Au} = 38.1$ nm, $n_{PMMA} = 1.488$ and $h_{PMMA} = 48$ nm (red curve).
S2. Basis Set of “Ideal” SPR Curves

A basis set of “ideal” SPR curves was constructed for use in obtaining best-fit thickness histograms for PMMA films with patterned channels. A subset of the basis set is shown in Figure S3 for a range of PMMA thicknesses $0 < h_{\text{PMMA}} < 60 \text{ nm}$. The increase in $h_{\text{PMMA}}$ results in a monotonic and nearly linear increase in the value of $\theta_i$ corresponding to the SPR minimum, as shown in Figure S4.

![Figure S3](image.png)

**Figure S3:** A subset of the basis set of “ideal” SPR curves used to obtain the best-fit thickness histograms for ROIs containing patterned PMMA channels. The curves were calculated for different thicknesses of PMMA using the best fit values for the index of refraction of PMMA ($n_{\text{PMMA}} = 1.4641$), the thickness and index of refraction of the gold film ($h_{\text{Au}} = 38.1 \text{ nm}$ and $n_{\text{Au}} = 0.1509 + 5.0755i$) and the index of refraction of the surrounding water ($n_{\text{water}} = 1.3332$), as determined from the best fit to the data shown in Figure S1. The thickness values corresponding to the different SPR curves are indicated in the inset, ranging from 0 nm (left) to 60 nm (right).
**Figure S4**: Plot of the value of $\theta_i$ (filled circles) and reflectivity (open circles) corresponding to the SPR minimum versus PMMA thickness for the basis set of “ideal” SPR curves for $0 < h_{PMMA} < 60$ nm.
S3. Residuals of Best Fits to SPR Curves

In Figure S5, we show the residuals, given by (measured reflectivity – best fit calculated reflectivity), for the data shown in Figures 4 – 7. It can be seen that the residuals are generally quite small (< $\pm$ 0.02 in reflectivity) over the entire range of angles of incidence $\theta_i$. For the data in Figure 5, corresponding to the SPR curve measured for the patterned PMMA film with channels perpendicular to the plane of incidence in the SPR experiment, the larger values of the residuals for 55° < $\theta_i$ < 58° could be due to a slight contamination of the sample surface.
**Figure S5**: Residuals of best fits to SPR data shown in (a) Figure 4, (b) Figure 5, (c) Figure 6, and (d) Figure 7. The residuals are calculated as (measured reflectivity – best fit calculated reflectivity). The different colored symbols in (c) and (d) correspond to the same color of symbol used in Figures 6 and 7.

**S4: Representative SPR Images**

In Figure S6, we show representative SPR images of the patterned PMMA sample. By dividing the image collected using $p$-polarized light by the image collected using $s$-polarized light as shown in (c), the effects of heterogeneities in the sample illumination are reduced. The SPR measurements shown in Figures 4 and 5 were performed on the central portion of the patterned area in the center of the images. The 400 µm × 420 µm area (20 lines, each 420 µm long, with a periodicity of 20 µm) corresponds to ~21 pixels (horizontal) × ~11 pixels (vertical), or an area per pixel of ~19 µm (horizontal) × ~38 µm (vertical). The ROIs used typically were typically ~12 pixels (horizontal) × 4 pixels (vertical).
Figure S6: Representative SPR images of the patterned PMMA sample and collected at an angle of incidence $\theta_i = 50^\circ$. (a) $p$-polarized light; (b) $s$-polarized light; and (c) the image collected using $p$-polarized light in (a) divided by the image collected using $s$-polarized light in (b). The dark rectangular features in the SPR images in (a) and (c) correspond to the different patterned regions of the sample with different areas and periodicities. By dividing the image collected using $p$-polarized light by the image collected using $s$-polarized light as shown in (c), the effects of heterogeneities in the sample illumination are reduced.

S5: Sensitivity of Average Thickness and Roughness to the Number and Thickness of Slabs Used to Model the Cellulose Coating

We have calculated the average thickness and roughness values assuming different numbers/thicknesses of slabs to model the cellulose coating, and we find that both the average thickness and roughness values are essentially independent of the number of slabs over a large range of slab thicknesses (Figure S7). Since the slopes on the plots in Figure S7 are essentially 1, the average thickness and roughness are independent of the number/thickness of the slabs used in the calculation, within this range. Although the average values are robust, we have kept a large number of thinner slabs to have the possibility of identifying single features with greater precision.
Figure S7: Comparison of best-fit average thickness and roughness for a cellulose microfibril-coated ROI for fits performed using basis sets of different number and thickness of slabs: 1 nm slabs with thickness \{0, 1, \ldots, 55\}, and 5 nm slabs with thickness \{0, 5, \ldots, 55\}. The straight red lines correspond to the best fit linear regression to the calculated data points, and the slope is very close to 1 in both (a) and (b).