In−Plane Resistivity of Ultrathin Gold Films: A High Sensitivity, Molecularly Differentiated Probe of Mercaptan Chemisorption at the Liquid−Metal Interface

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We report a high-precision resistivity measurement of mercaptan adsorption at the Au−liquid interface for Au films with thicknesses between the percolation threshold ($d \approx 5$ nm) and the electron mean free path ($d \approx 80$ nm).[1] A simple four-probe resistance measurement reveals a ca. 4% increase in the in-plane resistivity of a ∼40-nm thick Au film upon adsorption of mercaptan monolayers. The resistance measurement is inherently low-noise, enabling a detection limit of $\Gamma_{\min} \approx 1.4 \times 10^{-4}$ monolayer for $C_{16}H_{33}SH$. The effect is independent of the length of the alkyl chains of the chemisorbed alkanethiols, $C_nH_{2n+1}SH$ in the range $2 \leq n \leq 16$, but is dependent on the molecular character of the adsorbate.

This observation is germane, given the extensive interest in self-assembled monolayers (SAMs) of mercaptans on Au for fabrication of patterned structures.[2] Alkanethiol SAMs have been characterized by reflection−absorption infrared spectroscopy,[2c,3] surface plasmon resonance (SPR) measurements,[4] X-ray photoelectron spectroscopy,[2k,5] scanning tunneling microscopy,[6] atomic force microscopy,[7] electrochemistry,[8] surface acoustic wave devices,[9] contact angles,[2a] ellipsometry,[2a] radioactive labeling,[10] and so forth yet the need for a simple, fast, and nondestructive method to improve the detection limit of existing techniques is clear.

It was recognized as early as 1938 that the resistivity of ultrathin metal films is surface sensitive.[11a] Gas chemisorption typically increases the resistivity of thin metal films if the thickness, d, of the metal film is comparable to the electron mean free path.[11b,12] The accepted models proposed to explain these observations invoke nonspecular scattering of Fermi surface electron wave functions.[11b,c] Studies employing thin film resistivity changes at liquid−metal interfaces have been confined to monatomic adsorption,[13] while this work probes, for the first time, resistivity changes resulting from molecular adsorption.

Simultaneous SPR[14] and resistivity measurements were made during thiol[15] adsorption in a Teflon flow cell[16] by pressing the four contact wires directly onto the Au-coated prism surface with a Viton gasket. A Keithley model 244 current source operating at 15 mA and model 2001 low-noise multimeter were used to make four-point probe resistivity measurements. Temperature corrections to resistivity and SPR measurements were made using a thermistor installed immediately adjacent to the measurement region.

Figure 1 illustrates the simultaneously acquired SPR and resistivity responses upon introduction of 1 mM $C_{16}H_{25}SH$, the inset showing the approximately linear change in resistivity over the full range of coverage.[17] Of particular note is the excellent signal-to-noise ratio observed for the resistivity measurement.

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[15] Absolute ethanol was purified by agitation with fresh copper powder, followed by distillation. All thiols used in the experiment except where noted were purified by treatment with activated alumina before use. Benzenethiol, 4-mercaptophenol, 4-mercaptobenzoic acid, dodecanesulfonate, and pyridine were used as received. Au and Cr metals were 99.999% purity or better. Ozone (O_3) used in surface preparation was generated in an air−flow upstream of the cell using a Hg pen lamp.[4b] The flow rate was 25 mL/min, and $[O_3] = 0.5$ ppm, determined by an iodometric method.[4b]

[16] Gold films were deposited directly onto a Cr-coated (∼1 nm) equilateral prism (SF-10) substrate by thermal evaporation at ca. 0.05 nm/s at pressures below 1.5×10^{-6} Torr. The mass thickness of the gold was ∼50 nm as measured by profilometry. The prism substrate, Teflon cell, and all glassware used in the experiments were cleaned in freshly prepared 1: 4 H_2O_2: H_2SO_4 (Piranha) solution (**Caution**: Piranha solution should be handled carefully) for about 20 min, followed by rinsing in water (milli-Q UV-plus, 18.2 MΩ) and ethanol.

[17] A series of experiments with different thiol-terminated adsorbates demonstrated that (1) resistivity is linear with coverage, where coverage was determined by integrating the charge associated with the surface-bound Fc/Fc^{2+} redox reaction in $HSC_8H_{16}Fc$, at least up to 0.65 ML, (2) SPR resonance shift is linear with coverage, determined similarly, at least up to 0.65 ML, (3) SPR resonance shift is linear with coverage, as determined by infrared absorption for 4−mercaptobenzoic acid, over the full submonolayer to monolayer coverage range. The linearity of the SPR resonance shift with coverage has also been observed in (a) Sigal, G. B.; Mrksich, M.; Whitesides, G. M. *Langmuir* **1997**, *13*, 2749−2755. (b) Peterlinz, K. A.; Georgiadis, R. *Langmuir* **1996**, *12*, 4731−4740.

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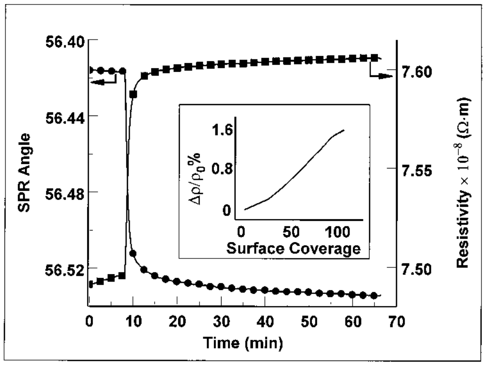

Figure 1. Position of the surface plasma resonance and in-plane resistivity (● and ■, respectively, every 15th point illustrated with a symbol) for a 50-nm thick Au film as a function of time before and after introduction of 1 mM $C_{16}H_{33}SH$ in ethanol in the flow cell. The inset illustrates the change in resistivity, expressed as $\Delta\rho/\rho_0$, as a function of surface coverage (%) over the full range of film assembly.

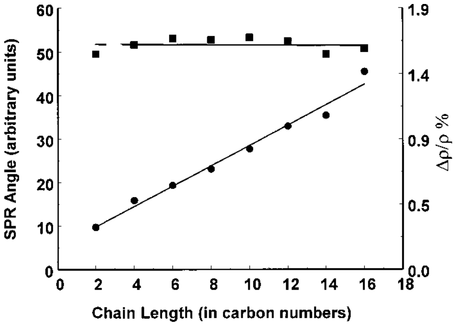

Figure 2. Full-scale changes in surface plasma resonance angle (●) and in-plane Au-film resistivity (■) for the assembly of full monolayers of n-alkanethiols ($C_nH_{2n+1}SH$) of increasing alkyl chain length (n) onto the same Au film. The lines are linear regression fits to the data.

Here a 40 mV cm^{-1} in-plane field results in a ca. 1.3 mV full-scale response for $C_{16}H_{25}SH$ assembly. The ca. ±100 nV fluctuation in the in-plane voltage results in a calculated detection limit for $C_nH_{2+1}SH$ chemisorption $\Delta\Gamma_{min} \approx 1.4 \times 10^{-4}$ monolayer for 40 nm Au. We were constrained to use ca. 50-nm Au films to obtain SPR data, but this geometry by no means optimizes sensitivity since thinner Au films clearly increase the magnitude of the in-plane voltage change and proportionally lower the detection limit. Furthermore, the Johnson noise limit for measurements at this bandwidth is ca. 0.5 nV at 300 K, so that the observed noise floor could potentially be lowered, resulting in further improvement in Γ_{min}. The $\Delta\Gamma_{min}$ measured improves on the most sensitive existing methods, the electrochemical Au-oxide stripping method,[8d,e] and is far superior to other methods.

Figure 2 shows the SPR and resistance responses to full monolayers formed from alkanethiols in the homologous series $C_nH_{2n+1}SH$, $2 \leq n \leq 16$. The SPR angle shift is proportional to the optical thickness of the SAM and, hence, to n[18] but the resistivity change is independent of chain length. These data suggest that for alkanethiols the increase in resistivity, $\Delta\rho/\rho_0$, is based on S-headgroup interactions with the Au and is less sensitive to nonbonded portions of the adsorbate molecule. This conclusion is supported by observations of different adsorbates, which naturally separate into three groups ordered according to the magnitude of $\Delta\rho/\rho_0$. On 40-nm films, alkanethiols produced the largest effect $\Delta\rho/\rho_0 = 0.0489 \pm 0.0008$, followed by para-substituted (HSϕR; R = H, OH, CO_2H) benzenethiols with $\Delta\rho/\rho_0 = 0.0438 \pm 0.0006$, and a last group, consisting of pyridine, phenoxide ion, and dodecanesulfonate, produced no observable change. It is especially notable that the reversible adsorption of pyridine from ethanol,[19] easily detectable via SPR, is undetectable by the in-plane resistivity measurement.

Resistivity differences among the three classes could originate from (a) different local or macroscopic, i.e., inclusive of larger scale missing molecule defects, surface density or (b) the extent of adsorbate electronic interaction with the Au film. The extent of electronic interaction offers a more likely explanation for the observed chemical differences.[20] Alkanethiols are known to adsorb on Au from ethanol as the alkanethiolate, which certainly involves transfer of electron density from the S headgroup to the Au.[21] However, the magnitude of transferred charge is small relative to that of native free electron density, $\Delta n/n \approx 0.001$,[22] and increasing n should decrease resistivity, opposite to the observed changes for all adsorbates. Thus, the effect is more likely to arise from the impact of surface dipoles on the diffuse scattering of charge carriers at the solid−liquid interface.[23] This explanation is consistent with the relative ordering of the three adsorbate classes, given the less polar Au−S bond for the aromatics, the independence of $\Delta\rho/\rho_0$ within the alkanethiolate series, and the absence of an effect for physisorbed, e.g., pyridine and phenoxide, and nonadsorbed, e.g., dodecanesulfonate, species.

In conclusion, in-plane resistivity is a novel high-precision probe for adsorption at the metal−liquid interface with a detection limit $\Gamma_{min} \approx 1.4 \times 10^{-4}$ monolayer for alkanethiol adsorption on Au from ethanol. For a given thin metal film, the magnitude of $\Delta\rho/\rho_0$ is dependent on the nature of the electronic interaction of the adsorbate headgroup with the Au but relatively insensitive to changes in electronic structure away from the binding atom.[24] The sensitivity, low noise, and ease of implementation suggest that in-plane conductivity measurements can be a powerful probe of specific adsorption at solid−liquid interfaces for conductive substrates thinner than an electron mean free path.

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