Self-Assembly Process of Organosulfur Molecular Layers on Gold Electrode: An *in situ* Ellipsometric and Electrochemical Study

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Electrochemical and ellipsometric measurements were made on gold surface while alkanethiols and organic disulfides were adsorbed. Anodic oxidation was observed to occur with molecular layer formation from thiols. Disulfide molecules appeared to oxidatively adsorb after reductive dissociation.

Self-assembled monolayers(SAMs) of organosulfur molecules on gold surface attracted much interest during the last decade.[1-3] Despite extensive investigations for their structures, studies by *in situ* methods such as ellipsometry on the *process* of self-assembly to elucidate the mechanism have been relatively scarce. We made *in situ* real-time ellipsometry and electrochemical measurements to gain an insight into the mechanism of adsorption and self-assembly of thiol and disulfide molecules.

A vacuum-deposited Au slide was used as a substrate for SAM formation. A small amount of a *n*-alkanethiol ($C_9H_{19}SH$, $C_{12}H_{25}SH$, or $C_{16}H_{33}SH$) or dipropyl disulfide was injected to 1.0 m*M* concentration into an acetonitrile solution. Changes in the ellipsometric parameters (Δ, Ψ)[4] of a polarized light reflected from the Au-solution interface were monitored on injection of the sulfur compound. A He-Ne laser light of 632.8 nm was used and the angle of incidence was 60°. The solution was stirred and deaerated with purified nitrogen during the measurements. Both Δ and Ψ decreased on injection of the adsorbate, sharply first then slowly, as shown in Figure 1 for (A) hexadecanethiol and (B) dipropyl disulfide. The big initial changes indicate that most of the adsorption process takes place rapidly, apart from the inevitable initial delay due to mass transport.

Figure 2 shows shifting potential of the gold electrode recorded simultaneously with the ellipsometry measurements. The solution used in this experiment was 0.10 *M* $LiClO_4$ in acetonitrile and the potential was recorded against an Ag/AgCl (3*M* NaCl) electrode. The presence of the supporting electrolyte did not affect the ellipsometric changes; hence the adsorption did not seem to be affected by the electrolyte. The open-circuit potential of gold dropped sharply by a thiol indicating an *anodic* reaction. The initial large and sharp drop was followed by a slow upward drift. Different alkanethiols gave similar results. On the other hand, the potential of gold rose slightly with dipropyl disulfide indicating a *cathodic* reaction.

When the Au electrode was potentiostatically fixed to an arbitrary potential in the range 0 ~ 500 mV, a current spike was observed on injection of the sulfur compounds. As shown in Figure 3, the current spikes were *anodic* in the case of thiols and *cathodic* with the disulfide adsorption. The magnitude of the current spike depended slightly on the potential chosen. The spikes had slowly decaying tails.

Self-assembly of an *n*-alkanethiol on Au has been considered by many workers to proceed by simple oxidative adsorption with production of molecular or atomic hydrogen as shown below[1-3].

$$RS\text{-}H + Au \rightarrow RS\text{-}Au + 1/2\,H_2 \qquad (1)$$

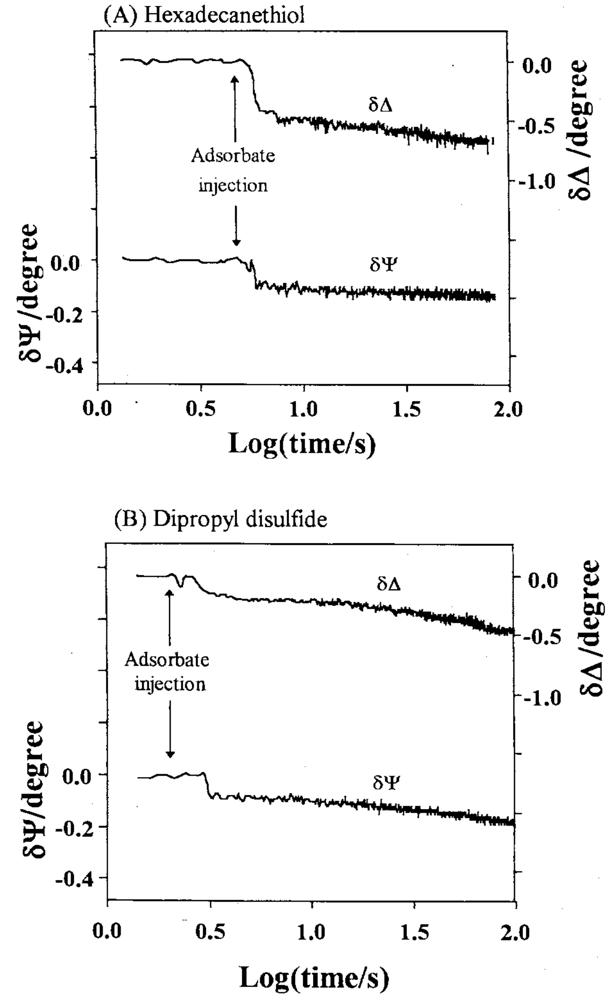

Figure 1. Changes in ellipsometric Δ and Ψ of gold surface on injection of organosulfur adsorbates to 1 m*M* concentration.

There have been reports of reversible desorption of SAM layer achieved by driving the potential of gold[5,6] or silver[7] to a negative value in strongly alkaline thiolate solutions. The observed current transients with the potentiostatic adsorption, the shifts of the open-circuit potential, and the reported electrochemical desorption clearly indicate that the adsorption of a neutral thiol is not a simple *chemical* process such as reaction (1). We propose an *electrochemical* oxidation mechanism for the adsorption of thiols as follows:

$$RSH + Au \rightarrow RS\text{-}Au + H^+ + e^-(Au) \qquad (2)$$

where $e^-(Au)$ represents an electron on gold metal. The anodic current spikes and the negative-going shift of open-circuit potential observed with SAM formation from thiols can be explained by the above anodic reaction. The slow upward drift of the potential after the initial sharp drop indicates a parasitic cathodic reaction that consumes the electron on the metal. The electron consuming parasitic reaction and the double layer charging account for the easy self-assembly in the absence of an electrochemical control. The open-circuit potential of gold is almost always in the range where reaction (2) is favored even in the absence of oxygen.

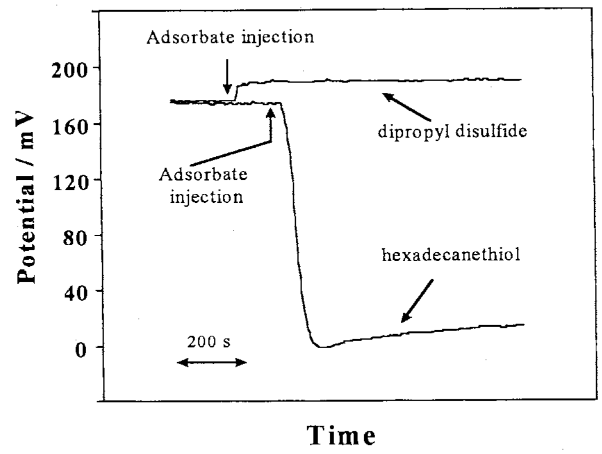

Figure 2. Changes of open circuit potential of gold with SAM formation from hexadecanethiol and dipropyl disulfide.

The SAM formation from dialkyl disulfide has been supposed to proceed by splitting of the S-S bond and gold-sulfur bond formation[2,3].

$$\text{RS-SR} + \text{AuAu} \rightarrow \text{RS-AuAu-SR}, \qquad (3)$$

However, such a chemical mechanism can not account for the potential shift and the current spike observed. The rise in the open-circuit potential and the negative current spikes observed with SAM formation from the disulfide are explained by the following mechanism which begins with a cathodic dissociation step immediately followed by an anodic adsorption step:

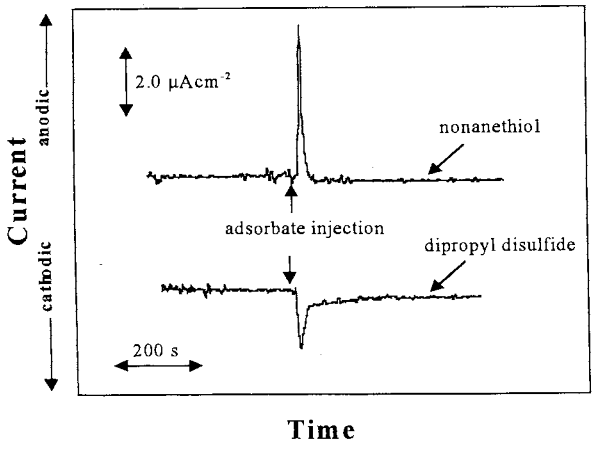

Figure 3. Transient currents observed with self-assembly of molecular layers at fixed potentials of gold.

$$\text{RSSR} + 2e^-(\text{Au}) \rightarrow 2\text{RS}^- \qquad (4)$$

$$(\text{or RSSR} + 2\text{H}^+ + 2e^-(\text{Au}) \rightarrow 2\text{RSH in the presence of H}^+)$$

$$\text{RS}^- + \text{Au} \rightarrow \text{RS-Au} + e^-(\text{Au}) \qquad (5)$$

$$(\text{or RSH} + \text{Au} \rightarrow \text{RS-Au} + \text{H}^+ + e^-(\text{Au}))$$

Part of the thiolate or thiol produced in the first process, reaction (4), is expected to diffuse away from the electrode, only a remaining fraction being oxidized in the following reaction (5). As a result, the overall current at the electrode should be cathodic, and the small rise of potential to the positive direction is also explained. Reorganization of the initially adsorbed layer and additional accommodation of the molecules can account for the slow drifts in the ellipsometric signals after the initial big changes and for the tails of the current peaks.

The potential drop of 0.18 V that appears in Figure 2 corresponds to 5.2 μC cm^{-2} if a double layer capacitance of 30 μ*F* cm^{-2} is assumed. This indicates that 5.4×10^{-11} mol cm^{-2} is adsorbed by reaction (2), which is an order of magnitude smaller than a complete monolayer. The charge associated with the current spikes such as in Figure 3 at a fixed potential is 42-56 μC cm^{-2}. This charge was expended to adsorb 4.4×10^{-10}-5.8×10^{-10} mol cm^{-2}. This is close to the complete coverage of 7.8×10^{-10} mol cm^{-2} calculated with data on Au(111)[8]. Evidently, in the open-circuit potential experiment, extensive fast adsorption is retarded by the negative shift of potential, whereas at a constant potential the adsorption by anodic oxidation is favored. Further studies are under way for more quantitative analysis.

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References and Notes

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