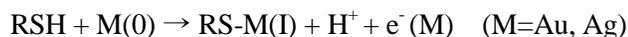


ELECTROCHEMICAL ADSORPTION MECHANISM OF
SELF-ASSEMBLING CARBOXYLIC ACIDS AND THIOLS
ON GOLD AND SILVER

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This report addresses the mechanism of adsorption of thiols and carboxylic acids on metals in the initial stage of forming a self-assembled monolayer (SAM). In previous recent studies, we investigated adsorption of the SAM-forming organosulfur compounds on gold and silver, by ellipsometry and electrochemical quartz crystal microgravimetry (EQCM).¹⁻⁴ The adsorption of thiols was found to occur through an anodic oxidation reaction that produce shift of the open circuit potential of the substrate metal in the negative direction, or an anodic current peak when the potential is fixed.



In the present study, adsorption of carboxylic acids on gold and silver electrodes was studied by electrochemical experiments to find a common feature in the reaction mechanism with that of thiol adsorption. Carboxylic acids spontaneously adsorb on silver, often to form SAMs, whereas adsorption on gold does not occur except when high potentials are applied to gold.^{5,6}

Adsorption of carboxylate ions seems to occur at gold surface through anodic reaction that is analogous to the reaction for thiol adsorption:



Adsorption on silver covered with oxidized layer occurs through replacement of oxide or hydroxide ions by carboxylate ions. When the silver surface is thoroughly reduced, an electrochemical reaction equivalent to the above reaction scheme can occur to result in carboxylate adsorbed on silver. Supporting evidences (open circuit potential shifts, reaction currents, etc.) of the reaction mechanism are presented and their implications are discussed. The difficulty of adsorption of organic acids on gold as compared to silver is understood by the high

potential of Au for oxidation to occur compared to Ag.

REFERENCES

1. S. Eu and W. Paik, *Chem. Lett.*, **1998**, 405.
2. S. Eu and W. Paik, *Mol. Cryst. Liq. Cryst.*, **337**, 49 (1999).
3. W. Paik, S. Eu, K. Lee, S. Chon, and M. Kim, *Langmuir*, 2000, **16**, 1019.
4. W. Paik, S. Eu, and K. Lee, *Electrochemical Society Meeting Abstract* **99-2**, No. 2205.
5. S. W. Han, S. W. Joo, T. H. Ha, Y. Kim, and K. Kim, *J. Phys. Chem. B*, 2000, **104**, 11987.
6. D. S. Corrigan, E. K. Krauskopf, L. M. Rice, A. Wieckowsky, and M. J. Weaver, *J. Phys. Chem.*, 1988, **92**, 1596.