

Adsorption Behavior of Triazinedithiol Derivatives Studied by Various Electrochemical Measurements

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Abstract: The self-assembled monolayer (SAMs)¹⁾ systems have been extensively investigated due to their potential applications in reforming a solid surface. It is well known that triazinedithiol derivatives (TAD) are excellent corrosion inhibitors for copper. However, the adsorption behaviors of such heterocyclic compounds containing nitrogen have been seldom reported. In our research, the adsorption behavior of 2-octylthio-1,3,5-triazine-4,6-dithiol monosodium (OTDS) on the surface of a Au monocrystalline electrode was characterized by various electrochemical measurements. The patterned electro/electroless Ni plating was accomplished on the copper substrate due to the OTDS SAM modification.

Experimental: The Au(111) electrode was made by the Clavilier method²⁾. The electrode was initially annealed and followed by quenching in ultrapure water. In this study, 2-octylthio-1,3,5-triazine-4,6-dithiol monosodium (OTDS) is the chemical being evaluated and 2-anilino-1,3,5-triazine-4,6-dithiol monosodium (ATDS) is used for comparison with OTDS. The occupied area per one TAD molecule on the electrode surface was estimated from cyclic voltammetry (CV) by calculating the quantity of electricity required for the oxidation-reduction reaction of OTDS. The adsorption amount change in the TAD with time was analyzed using a quartz crystal microbalance (QCM). In addition, the adsorption state of TAD was observed by scanning tunneling microscopy (STM).

A patterning examination during the electro/electroless plating was carried out by partially modifying the plating substrate with the TAD SAMs. The experimental conditions are summarized in Table 1.

Results and discussion: Fig. 1 shows the CV curves of the Au(111) monocrystalline electrode under different conditions. The peak around -0.8 V observed in both systems containing the additive is ascribed to the redox reaction of TAD. The occupied area per one OTDS molecule is calculated to be about 0.38 nm². This value is in good agreement with the molecular size of the OTDS molecule, suggesting that the OTDS SAM is formed. Fig. 2 shows the in-situ STM images of the Au(111) surface in 0.05 M HClO₄ after immersion in 0.5 mM OTDS solution for different times. The surface roughness gradually increases as the immersion time increases, implying that monolayer packing occurs.

It was found that the electronic conductivity of the electrode decreases after being covered with the OTDS SAM. On the basis of this experimental fact, the patterned electro/electroless Ni plating occurs on the copper substrate due to the OTDS modification, as illustrated in Fig. 3.

References

1) R. G. Nuzzo and D. L. Allara, *J. Am. Chem. Soc.*, **105**, 4481(1983).
2) J. Clavilier, R. Faure, G. Guinet, and R. Durand, *J. Electroanal. Chem.*, **107**, 205(1980).

Table 1 Bath composition and conditions for each plating.

For Ni electroplating		
NiSO ₄ · 6H ₂ O		0.64 M
Current density		1 A/dm ²
Bath temp.		25 °C
Plating time		20 sec.
Stirring rate		slow
OTDS modification (10 min.)		0.05 mM
For electroless NiP plating		
NiSO ₄ · 6H ₂ O		0.1 M
H ₂ NCH ₂ COOH		0.4 M
NaPH ₂ O ₂ · H ₂ O		0.25 M
pH (adjusted with 6 M H ₂ SO ₄ and 6 M KOH)		4.5
Bath temp.		70 °C
Plating time		210 sec.
Compressed Ar agitation		quiet
OTDS modification (60 min.)		0.05 mM
Catalyst	SnCl ₂	0.01 g/dm ³
	PdCl ₂	0.01 g/dm ³

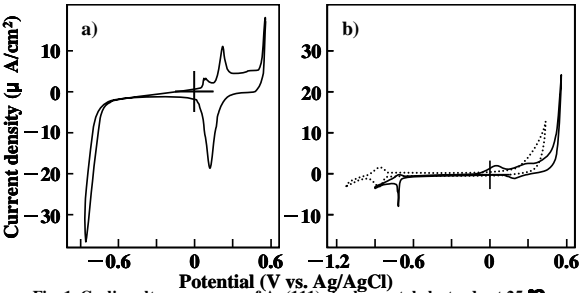


Fig. 1 Cyclic voltammograms of Au(111) single crystal electrode at 25 °C.
a) In 0.5 M KOH
b) Solid line: in 0.5 M KOH + 0.001 mM OTDS, broken line: in 0.5 M KOH + 0.5 mM ATDS. Sweep rate is 10 mV/s.

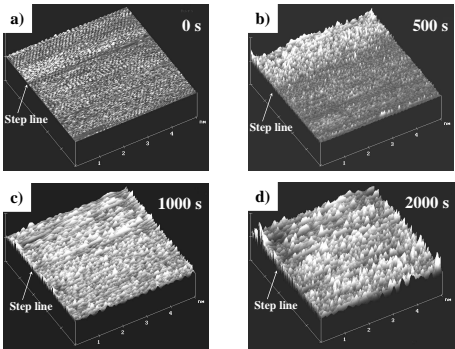


Fig. 2 In situ STM images of Au(111) single crystal electrode after immersion in 0.5 mM OTDS aqueous solution for a) 0 s, b) 500 s, c) 1000 s, d) 2000 s. Electrolyte solution: 0.05 M HClO₄, XY range: 5 nm

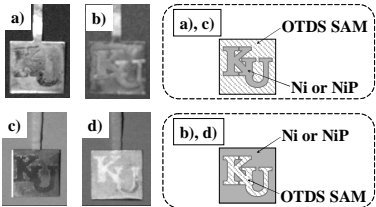


Fig. 3 Photographs of substrate after electro/electroless plating using Cu substrate treated by immersion in 0.5 mM OTDS aqueous solution.
a), b) Ni electrodeposited on Cu after immersion in solution for 10 min.
c), d) NiP electroless-deposited on Cu after immersion in solution for 60 min.