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DFT Analysis on Cathodic Reaction of Au Thiosulfate Complex at Au(111) Surface

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In order to achieve further precise control of electrodeposition processes, their reaction mechanisms should be well understood in molecular level. We have studied anodic reaction at the solid-liquid interface using DFT calculation to investigate the reaction mechanism of reducing agents in the electroless deposition process [1]. The next step is to elucidate cathodic part of the reaction mechanism; for example, it is necessary to understand deposition mechanism of Si in ionic liquid, involving impurity incorporation [2]. It is also important to elucidate the influence of coordinates on the deposition rate [3]. In this paper, we newly developed the theoretical model of the cathodic reaction.

The objective of the present work is to understand the effect of coordinates on the Au deposition process. To achieve this, cathodic reaction of Au^+ complex, which involves both complex dissociation and Au^+ deposition, was modeled to be analyzed with DFT. Thiosulfate ion, $S_2O_3^{2-}$, was chosen as a coordinate of Au^+ complex, which was strong candidate for the alternative to cyanide ion, CN^-. Furthermore, the reaction of Au^+ complex with $S_2O_3^{2-}$ was compared with the case of CN^-.

Cathodic reaction of Au^+ deposition was modeled and calculated as follows; First, Au^+ complexes, which are $[Au(S_2O_3)_2]^{3-}$ and $[Au(CN)_2]^-$, were adsorbed 0.5 nm above the Au(111) surface. The 0.5 nm distance is approximate maximum between the complex and metal surface, in which water molecule cannot enter. In this adsorption model, Au(111) surface was negatively charged by adding one electron, which would be accepted by Au^+ during the deposition. Second, sufficient numbers of water molecules as TIP4P model were settled above the Au(111) surface of the adsorption system using Monte-Carlo simulation. Then, the distance between Au^+ in complex and metal surface was gradually decreased so that the complex dissociated and Au^+ deposited on the surface.

The exchange-correlation functional used in DFT calculation was B3LYP. As basis sets, cc-pVDZ was assigned to S, O, N, C, and LANL2DZ was assigned to Au. The Au(111) surface was modeled as 2 layered cluster model which was consisted of 18 Au atoms.

Figure 1 shows energy profiles of the cathodic reaction of $[Au(S_2O_3)_2]^{3-}$ and $[Au(CN)_2]^-$. In this figure, the barrier of $[Au(S_2O_3)_2]^{3-}$ is much lower than that of $[Au(CN)_2]^-$, which corresponds to the result of potential sweep methods. This agreement shows the capability of our model in this time to reproduce the experimental behavior of Au^+ complexes.

Further detailed analyses indicated that the lower energy barrier of $[Au(S_2O_3)_2]^{3-}$ was caused by chemical characteristic of S in $S_2O_3^{2-}$; since S atom has larger outermost orbital, it exhibits high electron donation behavior to neighboring atoms. Such a tendency of S atom could stabilize the Au^+ cation with highly positive potential during the cleavage of Au-S bond of $[Au(S_2O_3)_2]^{3-}$.

As described above, this study shows details about the mechanism of Au deposition. The theoretical model constructed in this study is expected to be utilized for analysis on other important cathodic reaction, such as deposition of Si in ionic liquid.

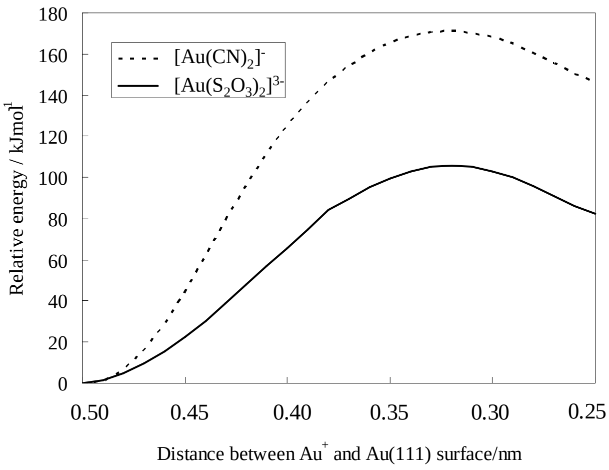

Figure 1. Energy profiles for cathodic reaction of Au cation complexes

References

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