Density Functional Theory Study on the Reaction Mechanism of Reductants for Electroless Silver Deposition Processes

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Electroless deposition processes are widely used in the various fields of microfabrication. In these processes, the electron is supplied by the oxidation reaction of the reductant. However, the reaction process is so complex that the mechanism has not been clarified yet. In this study, we employed Density Functional Theory (DFT) calculation to investigate the oxidation mechanism of representative reductants such as dimethylamine borane (DMAB), hypophosphite ion, and formaldehyde at the silver surface. This method has capability to provide quantitative evaluation of the oxidation mechanism at the elementary level, which cannot be achieved by the experimental approaches. Since the deposited metal surface should act as the catalyst for the oxidation reaction of reductants, we investigated the local interaction between silver surface and reductants by Energy Density Analysis (EDA) [1], which has capability to estimate the local energies of each atom composing the molecule.

All of the DFT calculations were performed using the B3LYP method as implemented in the GAUSSIAN 98 package. As for a model surface, we use $Ag_{22}(111)$ cluster (Fig. 1). Ag–Ag distance is fixed at its bulk lattice value of 2.889 Å. The Gaussian basis sets were 6-31G** for boron, phosphorous, carbon and hydrogen, 6-31+G** for oxygen in which diffuse functions, and Hay & Wadt for silver are argumented.

We investigated the oxidation reaction pathway of the three reductants at the silver surface. A general reaction pathway has been proposed by van den Meerakker, in which the reaction proceeds via three-coordinate intermediate species, initiated by dehydrogenation [2]. On the other hand, we have proposed an alternative pathway via five-coordinate species, initiated by addition of OH^- (Scheme 1) [3]. The results of the calculations suggested that the oxidation reaction of the three reductants at the silver surface took place via five-coordinate pathway rather than via three-coordinate one. It was also indicated that the rate-determining step of the five-coordinate pathway is the coordination of OH^- to the reductants adsorbed on the silver surface.

Then, the catalytic activity of the silver surface for the oxidation reaction of the reductants was investigated by the EDA. It was indicated that the energy level of the reductant part was high, that is, unstable, whereas that of the silver cluster part was low due to the adsorption. The total energy level calculated from the sum of both values also indicated the stable condition, as is seen in Fig. 2. It is expected that the exposed silver surface, which is under unstable condition, tends to be stabilized by the adsorption. It was also suggested that the adsorbed reductant was destabilized to obtain driving force to proceed to the next reaction step.

The rate-determining step, i. e., the coordination of OH^- was also analyzed in terms of adsorption geometry by the EDA. In the case of formaldehyde where the silver surface acts as a catalyst for the reaction, the OH^- and the reductant were destabilized at the silver cluster. On the other hand, smaller destabilization was observed from both OH^- and the reductant in the case of hypophosphite ion, where the silver surface does not act as a catalyst. It was considered that such a difference could be due to the difference of the adsorption geometry.

As described, we applied theoretical calculations to investigate the reaction mechanism of the electroless silver deposition processes and demonstrated that the favorable pathways of various reductants at the silver surface can be predicted in terms of the intermediates, and the factors of catalytic activity of metal surface can be also evaluated by the energy changes of each molecule.

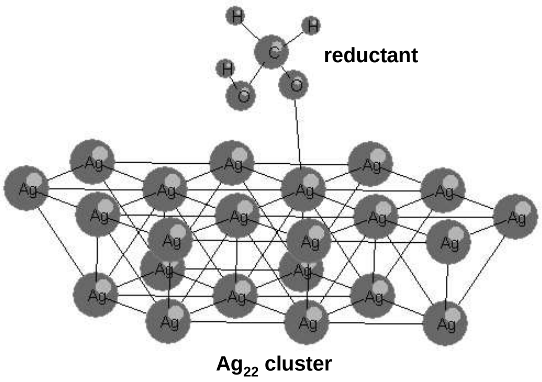

Fig. 1 Calculation model for reductant (intermediate of formaldehyde) adsorbed on the $Ag_{22}(111)$ cluster.

$$\underset{(1)}{\mathrm{RHX_3^-}}\xrightarrow{+\,\mathrm{OH^-}}\underset{(2)}{\mathrm{RHX_3(OH)^{2-}}}\xrightarrow[-e^-]{}\underset{(3)}{\mathrm{RHX_3(OH)^-}}\xrightarrow{-\mathrm{H}}\underset{(4)}{\mathrm{RX_3(OH)^-}}$$

R=formaldehyde:C, DMAB:B, hypophosphite ion:P X=H, O ,and/or OH

Scheme 1 Reaction pathway of reductants via five-coordinate intermediate.

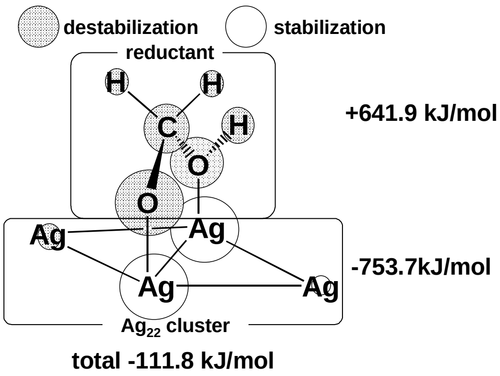

Fig. 2 Energy Density Analysis of formaldehyde (Scheme 1 (1)) adsorbed on the $Ag_{22}(111)$ cluster.

References

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