Graduate School of Advanced Science and Engineering,
Waseda University

# 博 士 論 文 概 要
## Doctor Thesis Synopsis

## 論 文 題 目
### Thesis Theme

# Nanoscale Analysis on the Reaction Mechanism of Reductants for Electroless Deposition Processes using Surface Enhanced Raman Spectroscopy

申 請 者
(Applicant Name)

| | |
|---|---|
| Bin | JIANG |
| 姜 | 彬 |

Major in Nanoscience and Nanoengineering,
Research on Nano-Functional Surface Chemistry

May, 2013

Electroless deposition process, which takes place with the deposition of metal by electron supplied by oxidation reaction of reductant, is significant for fabricating ultra-thin films and is widely applied for various fields such as microelectronics and nanotechnology. Since the process has advantages such as lower costs with simple processing, uniformity of deposits on complex shapes, independency on the electrical properties of the substrate and easy control of the coating thinness, it is expected as fundamental technology for micro and nano system fabrications.

In order to achieve more precise control of the solid-liquid interface in electroless deposition process to satisfy the strong demand for much advanced devices, it is necessary to clarify the reaction mechanism of electroless deposition process with molecular level resolution. However, the complexity of the reaction mechanism for reductant oxidation and other components such as complexing agent and additives in the process make it difficult to understand their chemistry in details. Such fundamental reaction mechanisms have not been fully elucidated yet. This often prevents researchers from understanding and establishing novel and highly controlled plating processes.

Against this background, Surface Enhanced Raman Scattering (SERS) effect, which is a breakthrough technique that can provide in-situ, ultrasensitive characterization of chemicals on metals down to sub-monolayer level for analysis of solid-liquid interface, has been utilized for many decades. In general, molecular level detection at solid-liquid interface by SERS sensors has been investigated by applying plasmonic metal either with roughened surfaces or nanostructures. An amplification of the Raman signal due to the electromagnetic field depends crucially on the size of the plasmonic metals and the distance from the plasmonic metals in the range of 1-2 nm. Thus, it is difficult to define the place where the detected molecules are existed.

This study attempts to understand the reaction mechanism of the electroless deposition process using experimental and theoretical methodologies focusing on the mechanism of the reductant reactions on metal surfaces. The experimental method is applicable for characterizing reductants adsorption on metal surfaces with high-selectivity component at right angle down to sub-monolayer level using a surface enhanced Raman antenna, which can define the place and structure of adsorbed reductants just only at 1-2 nm from the antenna surface. Meanwhile, the theoretical method Density Functional Theory (DFT) can provide molecular level, basic level information for understanding the mechanism according to the chemical characteristics. Much insight can be gained from the theoretical calculation, and the mere reproduction of experimental data will never be satisfying unless they come

with a great deal of improved understanding.

This thesis is composed of five chapters, as described below.

In chapter 1, general introduction regarding the electroless deposition process such as developments, analyses, and some examples of recent applications is overviewed. Considering some fundamental concepts about the reductants and catalytic activity of metal surfaces is also introduced. Moreover, the motivation for the entire study, the methodologies extremely useful for the analysis of the process and the fundamental strategy of this study are described.

In chapter 2, the measurement of several common reductants on metal plasmon antennas using SERS and DFT is described, which introduces the major premise that the function of the plasmon antenna and the agreement between experimental results and theoretical results is measured for the later chapters. In this chapter, the characterization of reductants adsorption on metal surfaces is given by using Surface Enhanced plasmon antenna. The antenna consists of a round pattern with coaxial dimples designed by Finite Difference Time Domain (FDTD) calculation to enhance the Raman scattering through the laser from the perpendicular direction to the surface. Furthermore, this antenna structure has very precipitous electric field at surface of the antenna. In order to utilize this precipitous electric field, we have applied piezo stage to realize the step by step measurement in changing the distance from the antenna with 1 nm/step. By using the plasmon antenna with the measurement of 1 nm step, Raman peaks of adsorbed reductants on metal surfaces were provided. Moreover, these peaks were only observed at 1-2 nm from the antenna surface which meant that this approach could define the structure of adsorbed reductants just only on the plasmon antenna. Meanwhile, the Raman spectra results were in good agreement with the DFT results of adsorption model of reductants on metal surfaces. These results suggest that this method creates a wide range of spin-off effects to the characterization of solid-liquid interface, and proposes an important basis for the analyses of the reaction mechanism of reductants on metal surfaces in the later chapters.

In chapter 3, the analysis of hydrazine and hypophosphite ions on a Cu surface with nano-scale resolution using SERS and DFT is determined, which is very useful for understanding the reaction mechanism of reductants in the electroless deposition. This chapter describes that we have previously reported on the fcc-Cu (111) underlayer with dual reductants of sodium hydrazine and hypophosphite for fabricating ultra-thin films with high perpendicular magnetic coercivities. Because $H_2PO_2^-$ was not oxidized to work as a reductant on the Cu surface in the electroless deposition of CoNiP, CoNiP nanodot arrays with high magnetic properties were

fabricated using an autocatalytic system with dual reductants $H_2PO_2^-$ and $N_2H_4$ in the previous study. The mechanism responsible for the enhancement of perpendicular magnetic coercivities has not been clearly established, however. Thus, we have attempted to characterize hydrazine and hypophosphite ions adsorption on a Cu surface to obtain fundamental knowledge about the mechanism by applying SERS and DFT calculations in this chapter. By using SERS and comparing the spectra to the results of DFT calculations, Raman peaks of adsorbed hydrazine and hypophosphite ions on Cu were identified. Furthermore, we examined the conformation of adsorbed hydrazine and hypophosphite ions on fcc-Cu (111) surface by DFT calculation. As a result, the mechanism of the interaction between hydrazine and hypophosphite ions on Cu surface, which is one of the most important steps for understanding the reaction mechanism of electroless deposition, has been predicted to explain the ultra-thin films with high perpendicular magnetic coercivities in our previous study.

In chapter 4, the analysis study of acceleration and suppression effect of thiourea on the oxidation reaction of hypophosphite ions on Ni surface using SERS and DFT is described, which is very important for understanding the complicated behavior of thiourea in the electroless deposition process as an additive. Our previous study has demonstrated that the acceleration effect of thiourea is mainly on the anodic reaction of the hypophosphite ions and the adsorption step is thought to be the most important effect. However, the acceleration and suppression mechanisms for the complicated behavior of thiourea in acidic/alkaline electroless plating bath has not been fully understood. In order to elucidate such mechanisms, this chapter has attempted to analyze the behavior of thiourea and hypophosphite ions adsorbed on Ni surface with nano-scale resolution using SERS and DFT calculations. By using SERS and comparing the spectra to the results of DFT calculations, the co-adsorption system and the molecular interaction between thiourea and hypophosphite ions on Ni surface were confirmed. Moreover, the acceleration effect or suppression effect of thiourea on the oxidation reaction of hypophosphite ions on Ni surface in acidic/alkaline bath were analyzed through an experimental view and a computational view. Consequently, an explanation that unifies both the acceleration and suppression mechanisms of thiourea in terms of its own fundamental characteristics has been proposed, and this will be a significant process for the analyses of the reaction mechanism of electroless deposition.

In chapter 5, the general conclusion showing the theory established through several analyses of this study is introduced. Some goals which the series of this study should achieve in the future are also described.

# 早稲田大学　博士（工学）　学位申請　研究業績書

**(List of research achievements for application of doctorate (Dr. of Engineering), Waseda University)**

氏 名　　　(姜 彬)　　　　　　　　　　印(　　　　　　　)

（As of October, 2013）

| 種 類 別 (By Type) | 題名、　　発表・発行掲載誌名、　　発表・発行年月、　　連名者（申請者含む） (theme, journal name, date & year of publication, name of authors inc. yourself) |
|---|---|
| ○ Original Article | <u>Bin Jiang</u>, Takanari Ouchi, Naofumi Shimano, Akira Otomo, Masahiro Kunimoto, Masahiro Yanagisawa, Takayuki Homma. "Analysis of hydrazine on a Cu surface with nanoscale resolution using surface enhanced Raman spectroscopy", *Electrochimica. Acta.*, 100 (2013), 317. |
| ○ Original Article | <u>Bin Jiang</u>, Siggi Wodarz, Masahiro Kunimoto, Masahiro Yanagisawa, Takayuki Homma. "Raman and DFT Study of the Reaction of Hydrazine and Hypophosphite on a Cu Surface in the Electroless Deposition Process", *Electrochemistry*, 81 (2013), 1. |
| ○ Original Article | <u>Bin Jiang</u>, Masahiro Kunimoto, Masahiro Yanagisawa, Takayuki Homma. "Effect of Thiourea on Oxidation of Hypophophsphite Ions on Ni Surface Investigated by Raman Spectroscopy and DFT Calculation", *J. Electrochem. Soc.*, 160 (2013), D366. |
| International Conference | <u>Bin Jiang</u>, Naofumi Shimano, Takanari Ouchi, Masahiro Yanagisawa, Takayuki Homma. Poster presentation on "Observation of Reductants on Copper surface in  Electroless Deposition Process with Nano-scale Resolution using Surface Enhanced Raman Spectroscopy", International symposiums on Renewable Energy & Materials Tailoring at Kyoto university, Kyoto, Japan, 18-19 Sept. 2011. |
| International Conference | <u>Bin Jiang</u>, Masahiro Kunimoto, Masahiro Yanagisawa, Takayuki Homma. Poster presentation on "Raman and DFT study of Reductant Adsorption on Metal Surfaces in Electroless Deposition Process", The PRiME 2012 joint international (222nd) meeting of the Electrochemical Societies, Hawaii Convention Center and the Hilton Hawaiian Village, Honolulu, Hawaii, USA, 7-12 Oct., 2012. |