Advances in Applied Physics, Vol. 4, 2016, no. 1, 51 - 58
HIKARI Ltd, www.m-hikari.com
https://doi.org/10.12988/aap.2016.6911

Reduction Position Controlled Electroless Silver Deposition on Glass Substrate via a Silver Seed Layer Itself

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Abstract

A new method for silver electroless deposition on glass substrate was developed based on silver itself as the seed layer. The seed layer was first reduced onto the glass surface by a spin-coated glucose layer. Then the silver thin island-like film was deposited electrolessly upon the seed layer by adding the glucose solution as a reducing agent. The seed layer morphology and the silver film were characterized using field emission scanning electron microscope (FE-SEM) and energy-dispersive X-ray analysis (EDX). This technique is the reduction position controlled (RPC) method of electroless deposition using a single solution composition set. It is an environmentally friendly *green* method that uses no harmful chemical substances.

Keywords: Optical properties of thin films; Electroless plating; Silver nanoparticles

1 Introduction

Nano-sized silver particle layers are required in many fields of industrial appli-

cations for use in main parts of electronic components, as in conductive ink, paste, and adhesives [6]. Furthermore, the diverse applications of nano-sized silver particle layers include surface-enhanced Raman scattering and surface-enhanced infrared absorption.

The various deposition methods of silver nanoparticle layers on substrates of many kinds include sputter deposition [15], oblique angle deposition [2], electroless deposition [11], chemical vapor deposition [16], photoinduced deposition [3], galvanic coating [5], chemical reduction [13], pulsed laser deposition [8], and thermal evaporation [7]. Electroless plating has received much attention as an alternative technique to vacuum evaporation for nanoparticle synthesis to nanoscale optics of many kinds [1]. A silver mirror (Tollen's) reaction [14], which is one kind of electroless deposition for silver layers, has been used widely for many years. However, Tollen's reaction is a method to produce a thick uniform film. It is difficult to apply it to produce a nanoparticle layer. To overcome this difficulty, a method using a seed layer has been developed. For electroless deposition, catalytic seed layer reliability was necessary because it is necessary to initiate electroless deposition. Reports of silver electroless deposition describe that palladium was used as the seed element [4, 10]. Palladium has good surface catalytic function. However, undesirable reaction steps invite Cl contamination. Furthermore, when a pure Ag film is required, Pd itself will have impurities. A way exists to restrain aggregation and particle growth using a protection molecule (citric acid, PVP, etc.) [9], but even though these molecules can be removed to a level with little difficulty, they pose a threat. Therefore, if possible, the use of these materials should be avoided. Using an exchange reaction between Ag ion and Si atom of the substrate using an acidic solution, a method exists to produce a Ag seed layer [12]. After seed formation, Tollen's solution was used. This approach is excellent because the adhesion between the Ag layer and the substrate is strong and elements or molecules other than Ag are not interposed. Nevertheless, it is regrettable that the substrate is limited (Si, etc.) and that the harmful HF is used.

We note that the defect of Tollen's reaction is a solution reaction. We have developed Reduction Position Controlled Deposition (RPCD) method, which restricts the seed reduction position at the surface. As described in this paper, it is a method for which silver itself was used as a seed layer. Other elements and molecules were not included in the silver seed layer. Furthermore, this method is a *green* method.

2 Experimental

Milli-Q water was used throughout the experiments. $AgNO_3$, NaOH, an aqueous solution of ammonium, and glucose were acquired as analytical grade reagents and were used without further purification. The solution concentration is shown respectively for each experiment. Micro-cover glass (18 mm × 18 mm; TROPHY) was used for substrate. The glasses were cleaned in an ultrasonically agitated isopropanol bath.

RPCD procedure

The RPCD method procedure is presented schematically in Fig. 1. First, the glucose layer was spin-coated as a reducing agent on the substrate. The dropping amount is 40 μl, rotation speed was 5400 rpm. After drying the glucose layer, ammoniacal silver nitrate solution (prepared by mixing an aqueous ammonia solution and silver nitrate solution) and aqueous sodium hydroxide of 40 μl were added dropwise, respectively, to create a seed layer. After formation of the seed layer, an aqueous glucose solution as a reducing agent of about 40 μl added to precipitate a silver reduction reaction. The substrate was washed with distilled water after the silver had precipitated.

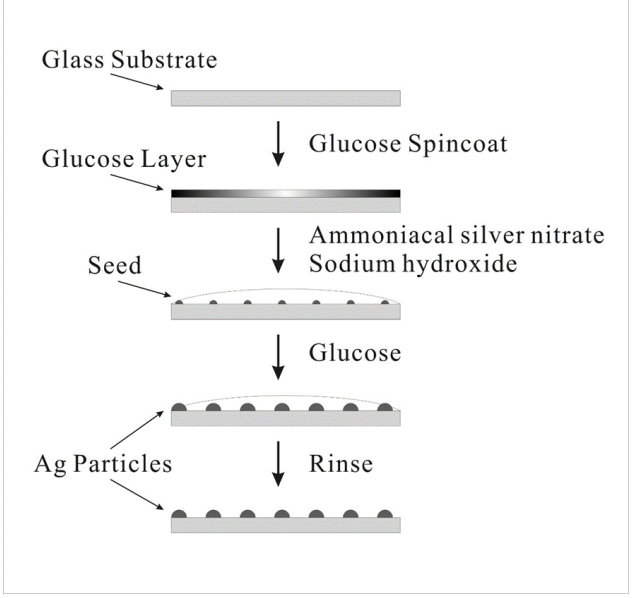

Figure 1. Schematic drawing of reduction position controlled (RPC) method.

Particle shape observation was performed using field emission scanning electron microscope (SEM, JSM-7000F; JEOL). Composition analysis of the particles was conducted using energy-dispersive X-ray spectrometry (EDX, JED-2300F; JEOL).

3 Results and Discussion

3.1 Ag Ion Concentration Dependence

The glucose concentration to form a reducing agent layer was constant (0.22 mol / mL), but the silver ion concentration to form a seed varied (Table 1). Concentrations of solutions forming the NP were fixed: silver nitrate 6.25 mol / mL, ammonia 0.09 mol / L, sodium hydroxide 0.01 mol / L and glucose 0.22 mol/ mL. The seed formation time was 10 min. Silver deposition time of 1 h produced a silver thin film.

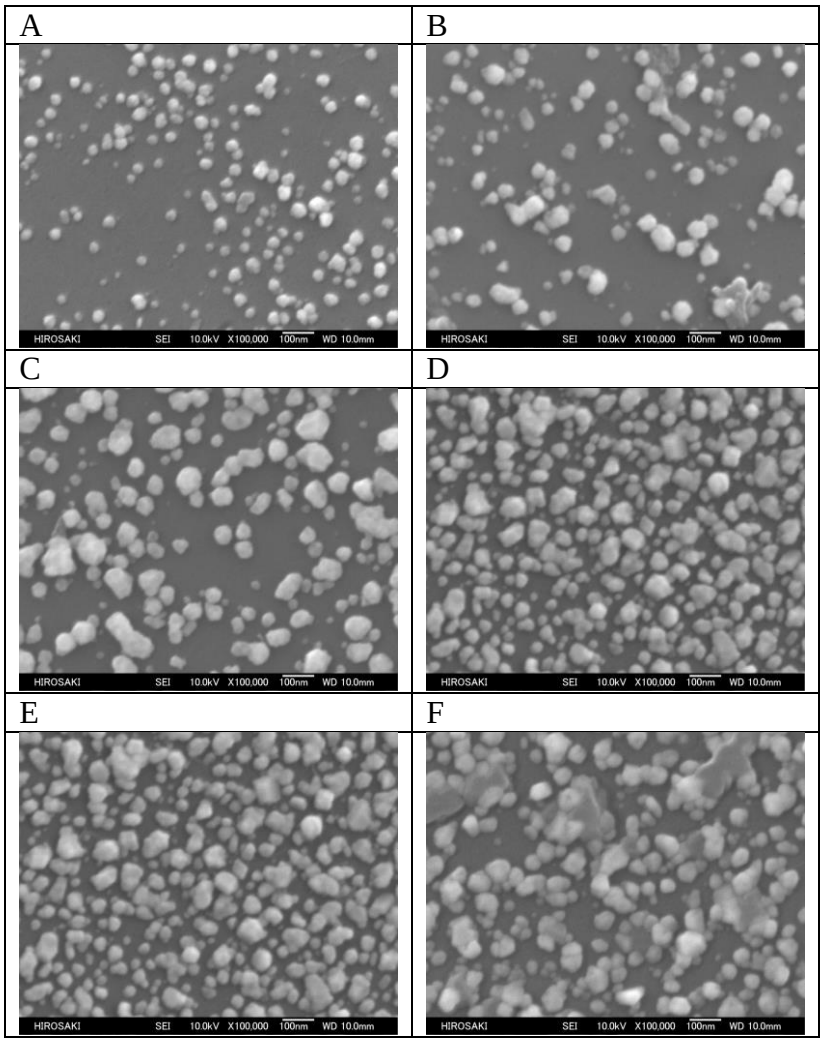

Figure 2. SEM images of the seed layer on glass (silver nitrate and ammonia are 0.0156 mol / mL and 0.0002 mol / L).

The SEM images in Fig. 2 show silver fine particle films produced by changing the solution concentration at NP layer formation. The compositions of the solutions we used are presented in Table 1. Results confirmed that the Ag particle size and Ag particle number differ depending on the silver ion concentration during seed layer formation. In A–C, low particle density Ag particle layers are shown as deposited. Dense layers with uniform particle size were obtained in D and E. In F, a layer is partially connected with a continuous-like film. Reducing the silver nitrate concentration during seed formation revealed that a fully equipped seed layer can be created. We have obtained Ag layers in various forms using this method. Silver (rather than a silver compound) deposition was confirmed using EDX.

Table 1. Concentrations of silver nitrate and ammonia for seed-layer formation

	silver nitrate (mol / mL)	ammonia (mol / L)
A	0.0156	0.0002
B	0.0208	0.0003
C	0.0313	0.0005
D	0.063	0.0009
E	0.125	0.0018
F	0.625	0.009

3.2 Glucose Layer Thickness Dependence

Next, an experiment was performed by particularly addressing the reducing agent layer thickness by varying the glucose concentration at spin coating, and by varying the thickness of the reducing agent layer. As the reducing agent layer becomes thinner, the amount of silver ions to be reduced decreases, which can be expected to create the resulting small seeds. The solution concentrations were the following: silver nitrate 6.25 mol / mL, ammonia 0.09 mol / L, sodium hydroxide 0.01 mol / L, and glucose 0.22 mol / mL. The glucose concentration at spin coating was varied between 0.002, 0.04, and 0.02 mol / L. Using seed formation time 10 min, silver deposition time 10 min, the results are presented in Fig. 3. Silver particles are deposited with more or less uniform sizes in all cases. In addition, as the reducing agent layer decreases, it is apparent that the particle size is also reduced. Moreover, the particle density is not changed much even if the particle size decreases. More or less uniform Ag particle layers are obtainable using this method, the number of particles and the particle size can be changed by varying the glucose concentration.

3.3 Silver nanoparticle size

By controlling the glucose layer thickness and Ag+ ion concentration during seed silver formation, we have produced Ag layers of particles having more or less uniform size. Figure 4 presents the silver particle sizes according to changes in the respective parameters. A thinner reducing agent layer produces a high-density layer of small particles. Reducing the amount of silver ions to be reduced at the time of seed formation prevents the formation of large particles. Then a layer of smaller particles is formed. For this study, concentrations of two solutions were varied independently.

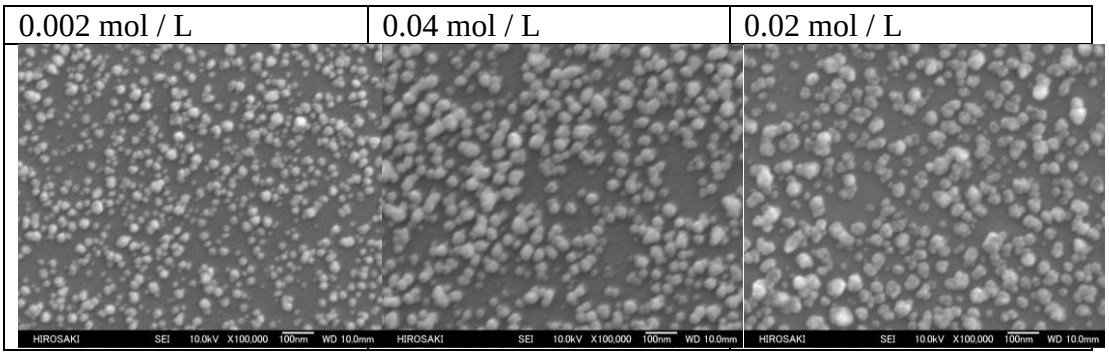

Figure 3. SEM images of silver fine particle films produced by the glucose concentration during spin coating

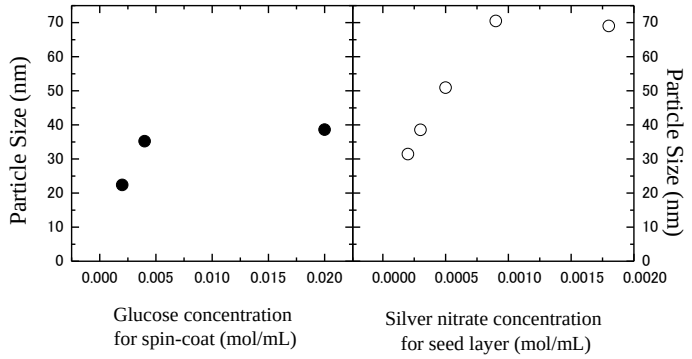

Figure 4. Silver particle size as a function of glucose concentration for spin-coat and silver nitrate concentration for seed layer formation.

4 Summary

We demonstrated a simple, green, and economical methodology for the facile preparation of Ag nanoparticles on a glass substrate. This methodology is based solely on reduction position control. Control of the reduction position formed a layer of fine silver particles on the glass using only Tollen's reagent. Varying the silver ion concentration and the reducing agent layer thickness during seed formation demonstrated that the size of deposited silver particles and the particle density can be controlled. This RPCD method described herein is an economical and environmentally benign process that requires no large-scale equipment or dangerous reagents.

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Received: September 21, 2016; Published: November 2, 2016