Full Length Article

# Nanoscale morphology of electrolessly deposited silver metal

Christopher N. Grabill[a], Daniel Freppon[a], Michelle Hettinger[a], Stephen M. Kuebler[a,b,*]

[a] *Chemistry Department, University of Central Florida, Orlando, FL 32816, USA*
[b] *CREOL, The College of Optics and Photonics, University of Central Florida, Orlando, FL 32816, USA*

A B S T R A C T

Electroless deposition of silver was studied to determine how chemical and physical parameters affect the morphology of the deposited metal. The study was conducted using variations of a silver deposition bath originally described by Danscher. The standard bath produced reflective and electrically conductive metal films comprised of agglomerates of small spheroidal nanoparticles. Removing gum arabic from the bath increased the deposition rate and changed the shape of the agglomerates but did not significantly change the size of the constituent nanoparticles. Replacing the citrate buffer with a dicarboxylate or monocarboxylate, which is less able to chelate $Ag^+$, produced surfaces comprised of larger, more faceted metal particles. The longevity of the bath varied with the choice of carboxylate. A new formulation buffered with maleate exhibited the highest stability, depositing silver for several hours without unwanted spontaneous formation of silver metal in solution. Optical measurements of electrolessly deposited films revealed absorptions associated with silver nanoparticles. Electrical measurements showed that the as-deposited films were five orders of magnitude less conductive than bulk silver, but low-temperature annealing increased the conductivity by four orders of magnitude.

## 1. Introduction

Noble metal nanostructures display fascinating phenomena such as surface-enhanced Raman scattering (SERS) [1], plasmon resonance absorption [2], and metal enhanced fluorescence [3]. These phenomena have attracted considerable attention and are becoming widely applied in several emerging technologies, including SERS microscopy [1,4], optical sensing [5], biological labeling [6], optical wave guiding on chips [7], and nano-optics [8]. Many reports indicate that these phenomena are sensitive to size, shape, and space between nanostructures of metal [9]. Controlling the surface nanoscale morphology of metal is thus required for these applications.

Colloidal metal-particle surfaces can be used for SERS, biosensing, and related applications [4,10]; but the instability of the metal surface due to the random agglomeration of colloidal metal limits their performance and widespread use [11]. An ideal metallization method would provide control over particle shape, size, orientation, and inter-particle spacing. Progress in this direction has been achieved. Vacuum evaporation and sputter-deposition of metal are widely used [9,12–15]. These techniques yield stable metal-particle films that are well packed, with controlled thickness [16]. Some approaches have been developed that afford improved control over particle size, shape, and surface functionalization [17–20].

For some applications, specific particle sizes are required to achieve the best performance. For instance, it has been shown that silver nanoparticles surfaces having a high surface roughness, so called "hot spots," can provide large surface enhancement when excited at optical frequencies [21–23]. Several teams have attempted to use high-temperature annealing of sputter-coated metal to control surface morphology [24,25]. However, the procedure itself is difficult to control, and high-temperature annealing can damage supporting substrates or devices. This is particularly true for micro-devices fabricated using soft-lithography technologies [26,27].

Electroless deposition (ED) is an alternative means for forming colloidal metallized surfaces and continuous conducting metallized surfaces under ambient conditions [28,29]. Unlike electroplating, ED can be achieved on a non-conducting surface because the metal is deposited from a bath that contains a source of the metal as a cation co-present with a chemical reducing agent. The ED bath is formulated to be metastable, so the reaction is thermodynamically spontaneous, but kinetically slow in solution. The ED reaction can be activated at a surface by attaching a nucleating species, typically a metal cation (e.g., $Sn^{2+}$, $Fe^{3+}$) or metal nano-particles [30–32]. ED starts at the nucleation sites forming a layer of silver particles. Silver particles formed by initial ED serve as nucleation sites that catalyze further deposition, so
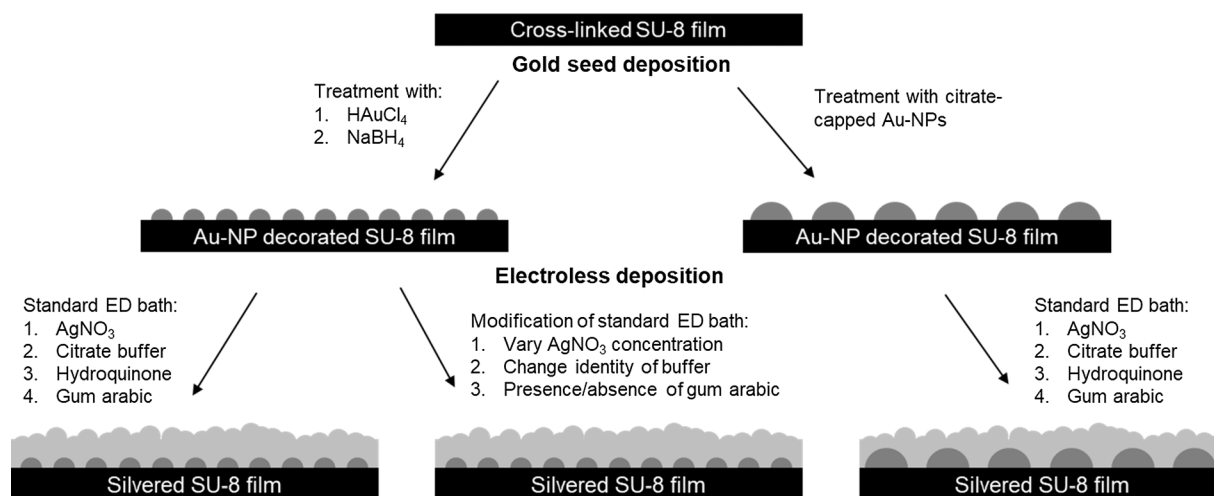
**Fig. 1.** Steps of electroless deposition (ED) of silver and parameters that were varied to investigate their impact on the morphology of the resulting metal layer.

the process continues forming an increasingly thick layer of metal with time. Some investigators have reported ways to control the size of silver particles formed by ED [33,34]. Yet to date, there is little understanding of how the shape, size, and nanoscale morphology of the electrolessly deposited metal depends upon the constituents of an ED-bath and the deposition condition.

Here we report an investigation of ED of silver based on a formulation first proposed by Danscher et al. [35] Fig. 1 is a schematic of the processing parameters explored in this study. Polymeric surfaces were prepared by spin-coating the cross-linkable epoxide SU-8 onto glass substrates [36]. The polymer samples were then treated with a bifunctional amine to which gold nanoparticles (NPs) could be attached to nucleate ED. The Au NP-seeded films were immersed in an ED bath, and the resulting silvered polymer films were examined using a variety of analytical techniques, including scanning electron microscopy (SEM), to characterize the nanoscale morphology. The procedure was repeated using a wide range of buffering agents, concentration of the silver ion, deposition times, and two types of Au NP seeds. The findings reported here show that the nanoscale morphology of the deposited silver depends sensitively on the constituents of the bath, the nature of the surface-bound nucleation species, and the deposition time, and that these parameters could be used to control the nanoscale morphology and obtain metallized surfaces with targeted physical and chemical properties.

## 2. Experimental methods

### 2.1. Preparation of polymer surfaces

Square 25 mm × 25 mm glass substrates were cleaned by immersing in aqueous 1.0 M aq. KOH (Fisher, CAS# 1310-58-3) for one hour, rinsing with copious deionized water, and drying in the oven at 100 °C for 15 min. The polymer surfaces were prepared by spin coating the cross-linkable epoxide SU-8 2035 resin (MicroChem) onto cleaned substrates (Ramp 1: 100 rpm s$^{-1}$, hold at 500 rpm for 10 s; Ramp 2: 300 rpm s$^{-1}$, hold at 4000 rpm for 30 s). The spin-coated films were baked at 65 °C for 3 min, followed by 95 °C for 6 min to remove residual solvent. Solvent-free films were then cured by irradiating for 3 min with a broad-band UV source (Loctite ZETA 7411-5, 400 W metal halide source, 315 nm –400 nm) through a long-pass filter (Omega Optical, PL-360LP, cut-off 360 nm) and then baking to complete the cross-linking (60 s at 65 °C, 15 min. at 95 °C, and 60 s at 65 °C).

### 2.2. Functionalization of polymer surface with bifunctional amines

The cross-linked SU-8 polymer surfaces were functionalized with bifunctional primary amines for subsequent binding of Au NPs. Amine functionalization was achieved by immersing cross-linked polymer films into a solution of 20 vol% 1,2-diaminoethane (Acros, CAS# 107-15-3) in ethanol for 60 min., rinsing with copious ethanol, then drying the samples in an oven at 100 °C for 15 min [36].

### 2.3. Functionalization of polymer surface with gold nanoparticles

Gold nanoparticles (Au NPs) were attached to amine-functionalized polymeric surfaces either by (1) binding Au$^{3+}$ cations to the amine sites and reducing with aqueous NaBH$_4$ (hereafter referred to as *in-situ* formation of Au NPs) or (2) separately preparing citrate-capped Au colloids and binding these to the amine sites. For *in-situ* formation of Au NPs, an amine-functionalized polymer film was immersed in $5.3 \times 10^{-4}$ M aqueous HAuCl$_4{}^-$ (Acros, CAS# 16961-25-4) for 30 min, rinsed with copious deionized water, immersed in 0.1 M aqueous NaBH$_4$ (Fisher, CAS# 16940-66-2) for 60 s, rinsed with again in deionized water, then allowed to dry by standing in air [37]. To functionalize polymeric surfaces with colloidal Au NPs, a suspension of the particles was first prepared following the method of Grabar et al. [38]. The amine-functionalized polymer films were then immersed into the gold colloid suspension for 60 min, rinsed with deionized water, then allowed to dry in air.

### 2.4. Silver electroless deposition

Silver deposition was achieved using a formulation originally reported by Danscher and co-workers [35], which is hereafter referred to as the "standard bath". The conditions were varied to explore how the nanoscale morphology of the deposited metal is affected by type of metallization bath, Ag$^+$ concentration, the type of carboxylate buffer, and the presence or absence of gum arabic. All ED was performed using polymer samples that were functionalized with *in situ*-produced Au NPs unless otherwise stated.

#### 2.4.1. Standard bath

A 33 wt% solution of gum arabic (Aldrich, CAS# 9000-01-5) was prepared by dissolving the material in hot deionized water, cooling, and filtering (0.45 μm pore size). A citrate buffer (pH = 3.8) was prepared consisting of 1.5 M citric acid (Aldrich, CAS# 5949-29-1) and 0.5 M trisodium citrate (Aldrich, CAS# 6132-04-3). An aqueous silver nitrate solution having a concentration of 222 mM was prepared by dissolving