Electroless silver plating on spin-coated silver nanoparticle seed layers

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Abstract

The electroless plating of silver films on pure silver nanoparticle seed layers prepared by spin-coating and thermal decomposition of PVP/Ag nanoparticle composite has been investigated. The plating results strongly depend on the agglomeration of nanoparticles and interparticle distances in the seed layer, which in turn crucially depend on the thermal processing parameters. Uniform nanocrystalline 200-nm-thick silver films on glass were prepared by plating on nanoparticle layers with surface density of $5.7 \times 10^{10}$ cm$^{-2}$ and average particle size of 40 nm. It is shown that electroless plating on nanoparticle seed layers can produce different surface structures and can finely tune the surface plasmon resonance in nanoparticle layers that can be useful for optical and sensing applications.

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1. Introduction

Electroless plating is a process in which a metal salt is reduced to metal on a surface from a solution without the use of an electrical potential [1]. This process has been widely utilized in coating many materials with metal films for numerous applications [2,3]. The popularity of this technique is due to its ease of use, its relatively quick results (usually less than 20 min), and uniform coatings. Electroless plating has attracted much attention as an alternative or supplemental technique to vacuum deposition and nanoparticle synthesis to fabricate micro- and nanoscale metallic structures for MEMS [4], surface plasmon resonance spectroscopy for DNA detection [5], surface-enhanced Raman spectroscopy (SERS) [6,7], and nanoscale optics [8,9].

Dielectric substrates such as glass must be catalytically activated prior to the plating to provide a surface that can interact with silver ions in solution causing their reduction on the surface and growth of the coating. The traditional method of electroless plating most commonly uses SnCl$_2$ and PdCl$_2$ as activators for this purpose. However, the Sn and Pd may be unwanted impurities for some applications of the electroless deposits. There is limited control over the microstructure and surface morphology of the deposits in this process.

There are several other approaches to activate the substrates for electroless plating. Tong et al. [10] have demonstrated the electroless plating of silver on silicon by using a seed layer of silver itself. Yang et al. [11] utilized Ag/Pd nanoparticle agglomerated nanostructures as templates for electroless copper deposition. Hrapovic et al. [12] prepared Au films by the reduction of a gold plating solution on a gold nanoparticle layer immobilized on an adhesive organic layer. Electroless plating on self-assembly monolayers on glass has been shown to be superior in durability over the Ag and Au films prepared by traditional procedures [13–15].

In present study, we prepared silver films by electroless plating on glass activated with pure Ag nanoparticle seed layers (NSLs). We consider this approach in fabricating templates for surface plasmon resonance (SPR) nanostructures [16]. We investigated the effects of the surface density of nanoparticles and thermal processing conditions of NSLs on the growth of the electroless silver films.

2. Experimental

Silver nanoparticle precursor solution used to form NSLs was prepared by reducing 0.16 g AgNO$_3$ in 30 ml of 2-
methoxyethanol in the presence of poly(vinyl)-N-pyrrolidone (PVP). The mass ratio of PVP (8000 g/mol) to AgNO₃ was 1:1. The mixture was kept at 90 °C until the color changes were no longer observed. The resulting colloidal solution was then removed from the hotplate and cooled in an ice bath.

Ultrasonically cleaned 20×20 mm², 0.2-mm-thick glass slides were covered with 0.1 mL of precursor solution, and spin-coated at 2000 rpm for 30 s to form the PVP/Ag nanoparticle composite layer. To form NSLs, the PVP/Ag-coated substrates were thermally processed by rapid heating to 420 °C in air to fully remove polymeric component, held at that temperature for different time intervals from 10 s to 2 min, and then removed from the heater for fast cooling. The spin-coating and thermal processing steps can be repeated several times to obtain denser surface coverage with nanoparticles.

Traditional activation of glass with SnCl₂ and PdCl₂ salts was performed for the comparison purposes. For surface activation, the substrates were kept consequently for several minutes in acidic 3.22×10⁻² M SnCl₂ (0.3 g SnCl₂, 0.1 mL HCl, 49.9 mL deionized water) and in 1.13×10⁻² M PdCl₂ (0.1 g PdCl₂, 0.1 mL HCl, 49.9 mL deionized water) solutions [1].

The plating solution was based on Tollén’s reagent, which consisted of two parts. The first part contained 0.03 g AgNO₃, 8.8 mL isopropanol, 1.14 mL acetic acid, and 40 mL 25% NH₄OH. The resulting concentration of silver ions was 3.5×10⁻² M. The second part contained 0.5 mL hydrazine as a reducing agent and 49.5 mL isopropanol. Both parts of the plating solution (7.5 mL of each) were mixed together, and the resulting solution was diluted with 15 mL of water to lower the concentration. The activated substrates were immersed each into the fresh plating solution for different time intervals from 1 to 15 min, extracted, rinsed in deionized water, and dried at room temperature.

The both NSLs and plated silver films were examined by means of optical spectroscopy, atomic force microscopy (AFM), and thin-film X-ray diffraction (XRD).

3. Results and discussion

Spin-coating of the nanoparticle precursor onto the glass substrate followed by the thermal decomposition of the polymeric matrix results in a uniform Ag NSL with the nanoparticle surface density of (2.1±0.2)×10¹⁰ cm⁻², lateral size of 35±10 nm, and average height of 12 nm (according to AFM measurements) after short-time annealing (5–20 s) at 420 °C. This layer appears pink in transmitted light with the SPR maximum at 496 nm. Longer annealing at that temperature leads to decrease in intensity of the SPR maximum and its shift to shorter wavelengths (down to 430 nm). This probably occurs due to a change in the shape of the particles, the increase in the interparticle distance, and further removal of the carbonaceous residue. Haynes and Duyne [17] have demonstrated that annealing of small metal islands increases their diameter-to-height (a/b) ratio and leads to blueshift of the SPR maximum by 200 nm. The decrease in the SPR intensity is related rather to the reduction of the number of nanoparticles due to their surface diffusion, agglomeration, and coalescence that results in a larger particle size. The increasing nanoparticle size should give the shift of SPR maximum to longer wavelengths [18], but the opposite trend dominates due to previously mentioned effects [19,20].

It should be noted that the size of the Ag nanoparticles in the PVP/Ag composite annealed at the temperature just below the PVP decomposition threshold is about 20±5 nm, height 7±2 nm, and the SPR maximum is centered at 430 nm. The nanoparticles in the NSL annealed at 420 °C for 10 s become larger due to the agglomeration and coalescence after the thermal decomposition of PVP. The volume of the individual particle is 3–4 times larger than that of the nanoparticle in the PVP/Ag composite annealed at lower temperature. The sizes of these nanoparticles corresponded to those measured from the width of silver XRD (111) peak.

![Fig. 1. Optical transmission spectra of Ag films plated on (a) single Ag NSL and (b) double Ag NSL, after different plating times; (c) AFM 2×2 μm² images of (from left to right) single NSL, double NSL, silver film plated for 3 min and 15 min on double NSL.](image-url)
The surface density of nanoparticles in double NSL was about \((5 \pm 0.5) \times 10^{10} \text{ cm}^{-2}\), and their average size was \(40 \pm 15 \text{ nm}\). The SPR maximum is centered at 508 nm and becomes broader, which indicates larger dispersion of particle sizes. The particles have the \(a/b\) ratio of 3.5 in this system. More particles have flat tops when compared with single NSL, which may be a result of particle agglomeration with the formation of flat islands. Although the particle \(a/b\) ratio becomes smaller, the particle size increases which leads to a slight redshift of the SPR maximum. The increase of the number of NSLs leads to only minor changes in the position of SPR maximum, but causes rougher and more opaque surface.

The thermal processing time of the NSL was critical in our experiments on electroless plating. Only very short annealing time (5–20 s) resulted in uniform deposition of the film. The films deposited on single NSLs annealed for 30–40 s were still discontinuous after 15 min of plating. There was almost no growth observed on single NSLs annealed for longer than 2 min. Only when the number of NSLs annealed for 2 min exceeds 3–4, the rough and discontinuous film forms during the plating. We focused mostly on short-time annealed NSLs.

The results of silver plating onto single and double NSLs are illustrated in Fig. 1. The nanoparticles had the \(a/b\) ratio of 3 and 3.5 for single and double layers, respectively. The SPR maximum shifts from 496 nm to 470 nm without change in the intensity after plating for 1 min upon a single NSL (Fig. 1a). This phenomenon is seen because the \(a/b\) ratio of seed particles decreases, which further indicates that the Ag film growth occurs faster in the direction normal to the substrate, at least initially. The growing islands must close the 50–80 nm wide gaps between the original seed particles. The width of the gaps determines the time needed to close them, and it requires approximately 3–6 min of deposition. The SPR maximum gradually deteriorates after 5 min of deposition due to the coalescence of growing islands. The SPR does not disappear completely even after 15 min of deposition, which may be attributed to a degree of discontinuity in the film [21]. The maximum at 350 nm becomes more pronounced, probably as a result of quadrupole resonance in larger oblate islands [19] or the void resonance [22].

By comparing the optical spectra in Fig. 1a and b, one can see that 1-min plating on the double NSL is required to obtain the same result as for the 5-min plating on the single layer. We have found that on the double NSL, the particle lateral size increases to 90–100 nm and the height increases to 30–35 nm after 3 min of plating (Fig. 1c). The estimated lateral growth rate, therefore, is 7–8 nm/min in our experimental conditions. This could give an opportunity to precisely adjust the nanoparticle size, and to form the specific film morphology. The film growth rate normal to the substrate is estimated at 10–15 nm/min. The gap between the nanoparticles is 10–25 nm in the double NSL (Fig. 1c), and therefore it takes only 0.5–1.5 min to close it as supported by the experimental data. The film thickness was approximately 200 nm after 15 min of deposition on both the single and double NSLs. The surface morphology and optical spectra were also very similar.

The grain size of Ag films plated on the NSLs strongly depends on the number of layers. This parameter influences the agglomeration of
nanoparticles and surface morphology of the NSL, which in turn affects the morphology of the plated film. Fig. 2a–c shows several examples of surface morphology of films deposited under the same conditions on differently treated NSLs. In Fig. 2a, a modified thermal processing procedure of a relatively thick single PVP/Ag composite layer resulted in a nearly continuous Ag film without noticeable SPR, probably owing to higher concentration of nanoparticles and their more efficient agglomeration and coalescence. Electroless plating on that layer produced uniform silver film with low roughness (RMS 9.3 nm) and the grain size in the range of 130–170 nm according to AFM.

In Fig. 2b, a triple NSL was deposited, and each layer annealed for 10 s. It had slightly higher substrate coverage than the double NSL in Figs. 2c and 1c, but also larger particle size and broader particle size distribution. This resulted in larger grain size, surface roughness (RMS 16.5 nm), and higher porosity of the plated film. The plating on double NSL produced the film surface morphology similar to the deposition on a traditional Sn–Pd activation layer. The resulting 200-nm-thick films in both cases are polycrystalline with the grain size of 80–90 nm, surface roughness RMS 13.8 nm and 10.1 nm, respectively, and good electrical conductivity.

The gap width between nanoparticles in the NSL is a very limiting factor in the formation of silver film during electroless plating. There was no film formed if a single NSL was annealed for more than 120 s at 420 °C. When the plating was performed on the multiple (3–5) NSLs with each layer annealed for 30–120 s, a discontinuous, rough film was formed. Therefore, it may be possible to apply electroless plating for fabrication of metal structures with interesting architectures and properties by controlling nanoparticle distribution on the substrate surface. Fig. 3a shows the optical spectrum of a double NSL prepared by subsequent annealing of the first layer for 120 s (usually weaker SPR maximum at 430 nm) and second layer for 10 s (usually stronger SPR maximum at 500 nm). Both SPR maxima can be seen in Fig. 3a, indicating that the individuality of each layer is maintained. The immersion of this sample in Ag plating solution did not produce a continuous film, as was observed for short-time annealed single NSL. Instead, a transparent material with a strong broad SPR maximum was formed (Fig. 3b and the AFM image of the corresponding surface). The average height of the particle agglomerates seen in the AFM image is 110 nm. This indicates mostly vertical growth (6–7 nm/min) of Ag islands during the plating. It is possible that agglomeration of nanoparticles in the second NSL around the smaller amount of larger nanoparticles in the first layer could create specific conditions for such growth. It is also possible that secondary nucleation of silver nanoparticles from the plating solution occurred on the NSL in this case. This could explain the SPR enhancement.

4. Summary

Our experiments have shown that electroless plating of silver occurs readily on the pure silver nanoparticle seed layer formed by spin-coating and thermal decomposition of the initial PVP/Ag nanoparticle composite. The increase in the surface density of nanoparticles results in less porous nanocrystalline films. Uniform, smooth nanocrystalline ~200-nm-thick silver films were prepared on NSLs with surface density of $5.7 \times 10^{10}$ cm$^{-2}$ and average particle size of 40 nm.

The parameters of thermal processing of the PVP/Ag nanoparticle composite are critical for the formation of the NSL and plated silver film. The heating rate, annealing temperature and time determine the NSL architecture that can vary from uniform Ag nanoparticle layer through various agglomerated structures to a nearly continuous film. We have found that it is possible to control the plated film microstructure and surface morphology by using different combinations of nanoparticle sizes in the NSL, its annealing time and temperature, and different plating times. The investigated approach can be useful in fabrication of metal micro- and nanostructures with controlled properties for a number of applications.

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References
