

Activation of Ag Nanoparticle Catalysts and Stabilization of Electroless Cu Plating Bath by Sodium Citrate

Takanori SUGAYA^a, Yutaka FUJIWARA^{b,*}, Yasuyuki KOBAYASHI^b,
Atsushi KOISHIKAWA^a, Yasuhiro HOSHIYAMA^c and Hidekazu MIYAKE^c

^a Graduate School of Engineering, Kansai University(3-3-35, Yamate-cho, Suita-shi, Osaka 564-8680)

^b Osaka Municipal Technical Research Institute(1-6-50, Morinomiya, Joto-ku, Osaka-shi, Osaka 536-8553)

^c Faculty of Chemistry, Materials and Bioengineering, Kansai University(3-3-35, Yamate-cho, Suita-shi, Osaka 564-8680)

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1. Introduction

Electroless Cu plating on polymer substrates such as epoxy or polyimide is important in printed wiring board manufacturing^{1,2)}. Among pretreatment processes for the electroless plating, catalyzing processes using Pd/Sn mixed colloids are necessary to initiate the electroless plating³⁾. However, the Pd/Sn mixed colloid catalysts present some disadvantages for fabricating the narrower circuit lines at lower cost⁴⁾. For example, residual Pd beneath the photoresist decreases the insulation.

Ag nanoparticle colloidal solutions are effective as alternative catalysts to the Pd/Sn mixed colloids^{4)~7)}. We proposed a facile preparation process of Ag nanoparticle colloidal solutions⁷⁾, and showed the catalytic activities of nanoparticles for electroless Cu plating^{8),9)}. Results suggested that the acceleration process using an acidic solution, which is necessary to activate the Pd/Sn catalysts, is not necessary in the Ag nanoparticle catalyst processes^{7),10)}. We also proposed substrate conditioning processes to promote nanoparticles adsorption^{7),9),10)}.

We present here the post-treatment of the Ag nanoparticle adsorbed substrates using a sodium citrate solution at a neutral pH. The post-treatment stabilizes the adsorbed nanoparticles and enhances the catalytic activity for electroless Cu plating.

2. Experimental

Cu-clad epoxy boards (FR-4, Sunhayato), the Cu layers of which were removed chemically by 0.9 mol dm⁻³ ammonium peroxodisulfate solution at 50 °C, were used as substrates unless otherwise noted. As the conditioning process to promote the adsorption of Ag nanoparticles, the substrates were dipped in a poly(diallyldimethylammonium chloride) (PDDA, 20 mass% in water, Mw = 200,000-350,000, Aldrich) solution for 300 s, which has a quaternary amine concentration of 0.1 mol dm⁻³¹⁰⁾. After conditioning, the substrates were rinsed with water and were dipped in a Ag nanoparticle colloidal solution for 300 s.

The Ag nanoparticle colloidal solutions were prepared by reducing Ag⁺ ions with Sn(II)-citrate complex⁷⁾. Reagent grade chemicals of SnSO₄, trisodium citrate dihydrate, and AgNO₃ were used as received. The Ag nanoparticle colloidal solutions contained 0.01 mol dm⁻³ Ag, 0.1 mol dm⁻³ total Sn and 0.2 mol dm⁻³ total citrate.

The solution pH was not adjusted: it was 5.1.

The Ag nanoparticle adsorbed substrates were dipped in a 0.1 mol dm⁻³ trisodium citrate solution at pH 8.0 for 60 s as the post treatment. Post-treatment using 1 mol dm⁻³ H₂SO₄ was performed, which is indispensable for the Pd/Sn catalysts to enhance their catalytic activity³⁾. The conditioning, adsorption and post-treatment processes were carried out at room temperature with mild stirring.

Amounts of the adsorbed Ag and Sn were determined using an inductively coupled plasma - atomic emission spectrometer (ICP-AES, ICPS-8100; Shimadzu), after dissolving in a HNO₃ solution.

Morphology of the adsorbed Ag nanoparticles on a Corning #1737 glass substrate was examined with an atomic force microscope (AFM, Digital Instrument Nanoscope IIIa). The adsorbed Ag nanoparticle diameters were evaluated from the plan-view AFM images using a WinROOF image analysis system.

Electroless Cu plating onto the Ag nanoparticle adsorbed epoxy substrates was conducted using a proprietary plating solution of MOON Copper (Okuno Chemical) at 45 °C. The amount of the deposited Cu was determined from X-ray fluorescent spectra (RIX 3100, Rh K α ; Rigaku).

Stability of the Ag nanoparticles adsorbed onto the epoxy substrate was evaluated by determining the amount of Ag and Sn desorbed from the 103 cm² substrate into a 0.1 dm³ plating bath at 45 °C in 60 s. The desorbed amounts were determined by ICP-AES after the HNO₃ addition.

3. Results and Discussion

The amounts of Ag and Sn on the epoxy substrates are shown in **Fig. 1** with empty bars. Filled bars show those desorbed from the substrates in an electroless Cu plating bath.

Onto the conditioned epoxy substrates, Ag and Sn of about 4 μ g cm⁻² and 1 μ g cm⁻² were adsorbed. The Ag nanoparticle diameter was around 5 nm⁷⁾. When the 5-nm-diameter Ag spheres are adsorbed most closely, their amount is calculated to be 3.2 μ g cm⁻². Therefore, the adsorbed amounts almost correspond to one monolayer adsorption of the nanoparticles.

The post-treatment with citrate slightly decreased the adsorbed amounts of Ag but significantly decreased those of Sn to about 20 % of their initial values. These changes in the adsorbed amounts resemble those caused by the post-treatment with H₂SO₄. In the Pd/Sn mixed colloid catalyst processes, the post-treatment with acid is necessary to activate the catalysts by desorbing the

* E-mail: fujiwara@omtri.or.jp

excess Sn³). Therefore, the post-treatment with citrate is expected to enhance the catalytic activity for the electroless Cu plating.

Fig. 2 depicts the AFM images of the glass substrate and the adsorbed Ag nanoparticles on the conditioned substrates. The Ag nanoparticles wholly covered the substrate surface with no wide gaps or large holes. The average diameter and the standard deviation of the adsorbed particles were, respectively, 23.7 nm and 3.2 nm. Although the adsorbed amounts of Ag shown in **Fig. 1** suggest the monolayer adsorption of the nanoparticles, the average diameter was markedly larger than that in the colloidal solution. Therefore, the particles shown in the AFM image probably reflect loosely aggregated two-dimensional domains of the adsorbed Ag nanoparticles.

The post-treatment with citrate did not decrease the high surface coverage of the adsorbed Ag nanoparticles, but slightly increased the size of the domains to 25.8 ± 4.7 nm. Three-dimensional

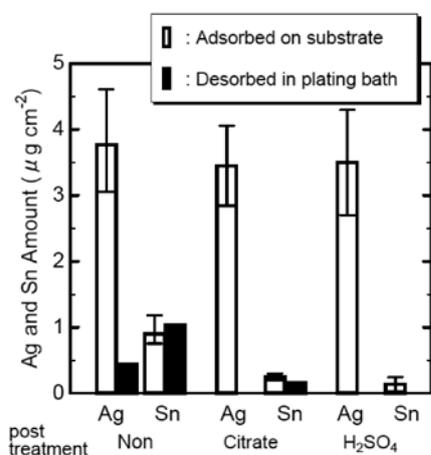


Fig. 1 Amounts of Ag and Sn adsorbed onto conditioned epoxy substrates (empty bars) and those desorbed in electroless Cu plating bath in 60 s (filled bars).

aggregation of particles was observed in places.

In contrast, the post-treatment with H₂SO₄ significantly increased the domain size to 36.8 ± 5.6 nm. Three-dimensional aggregation of particles and wide gaps were observed, which suggests that Ag nanoparticles were partly dissolved in the H₂SO₄ solution and Ag was deposited again to grow the Ag grains.

Fig. 3 shows the amounts of electroless Cu deposited on the Ag nanoparticle adsorbed epoxy substrates with and without post-treatment. The amount of Cu deposited on the substrates post-treated with citrate was larger than those on the substrates without post-treatment at any deposition time. This acceleration effect is attributed to the decrease in the induction time to establish the constant deposition rate by complete coverage of the deposited Cu¹¹). The decrease in the induction time is probably caused by the decrease in the adsorbed Sn shown in **Fig. 1**, similarly to the activation effects of the post-treatment with acid in the Pd/Sn mixed colloid catalyst processes³).

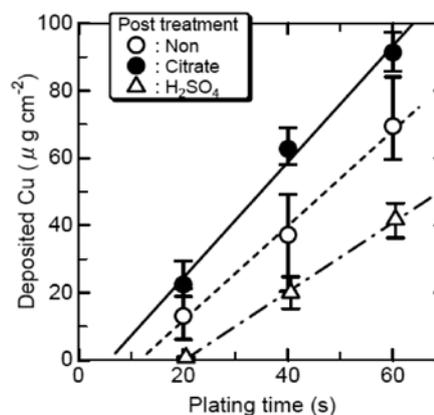


Fig. 3 Amounts of electrolessly deposited Cu on Ag nanoparticle adsorbed epoxy substrates with and without post-treatments as a function of plating time.

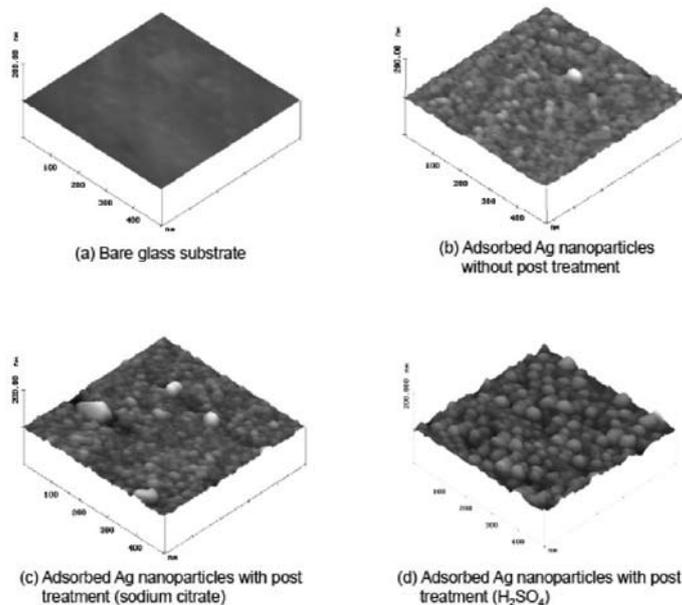


Fig. 2 AFM images of adsorbed Ag nanoparticles on glass substrates with and without post-treatments.

AFM images of Corning #1737 glass substrate (a), and adsorbed Ag nanoparticles with and without post-treatments (b, c, d).

The amount of Cu deposited on the substrates post-treated with H₂SO₄ was smaller than those on the substrates without post-treatment at any deposition time, probably because of the decrease in the active surface area of the adsorbed Ag nanoparticles caused by grain coarsening shown in **Fig. 2**.

The amounts of Ag and Sn desorbed from the substrates in an electroless Cu plating bath in 60 s are shown with the filled bars in **Fig. 1**. Sn was fully desorbed in the plating bath from the substrate without post-treatments, although about 90 % of the adsorbed Ag stayed at the substrate surface. This shows that the SnO₂ shell of the particles was fully dissolved in the plating bath¹²⁾. Electroless Cu plating, therefore, started at the Ag nanoparticle adsorbed substrates with no acceleration processes, as shown in **Fig. 3**.

The Ag nanoparticles were partly desorbed from the substrates without post-treatments but wholly stayed at the post-treated substrate surfaces, as can be seen from **Fig. 1**. Prevention of the Ag nanoparticle desorption by post-treatments stabilized the plating baths. Actually, the plating bath decomposition was not observed when the substrate was post-treated with sodium citrate or H₂SO₄. However, the plating bath was decomposed in 300 s after the 120 s electroless Cu plating using the substrates without post-treatments. The desorbed Ag nanoparticles acted as the nuclei at which the electroless deposition started, and caused the bath decomposition, *i.e.*, the Cu particle precipitation.

In conclusion, the post-treatment of the Ag nanoparticle adsorbed substrates with citrate accelerated the electroless Cu plating and

prevented the plating bath decomposition.

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