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Novel Cyanide-Free Au Electroless Deposition with Controllable Adhesion to Plastic Films

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Introduction :

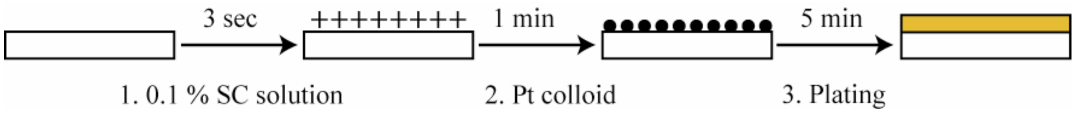
Electroless plating is a chemical deposition technique in which metal is deposited on insulating substrates without the use of electricity. We have reported that Pd nanoparticles embedded in polymer films works as an excellent catalyst for initiation of the electroless plating reactions, where Ni-P and ZnO thin film depositions with site selectivity were demonstrated.[1,2)] Gold electroless plating is in particular important and indispensable due to its various excellent characteristics such as high electrical conductivity, high corrosion resistance and brilliant appearance, in spite of its high price. However, highly toxic gold cyanide has been used for the conventional electroless Au plating and also highly toxic potassium cyanide is produced as a by-product.[3)]

$$NaBH_3OH + 3KAu(CN)_2 + 3KOH \rightarrow NaBO_2 + 3Au + \frac{3}{2}H_2 + 2H_2O + 6KCN \qquad (1)$$

Therefore, this process is unfavorable for the management of working safety and global environments. In addition, complex surface modification processes were required to achieve high adhesion of the plated metal films to substrates. The aim of this work is to develop a simple electroless plating method using metal colloids as catalysts to offer high adhesion without conventional surface modification processes.

Experimental :

Pt colloid was prepared by the reduction of $H_2PtCl_6{\cdot}H_2O$ (20 mM) by $NaBH_4$ (40 mM) with the presence of 1 wt% polyvynlypyrrodidone (PVP) at room temperature for 1 day. The immobilization of the Pt nanoparticles on a substrate and the subsequent Au electroless plating were carried out as shown in Scheme 1. A polymer film was immersed in 0.1 % stearyl trimethly ammonium chloride (SC) aqueous solution for a few seconds. Then the film with surface positively surface was immersed into the Pt colloid for 1 min to immobilized the Pt nanopartcles on the surface. Then, the film was immersed in the Au plating bath composed of 20 mM $HAuCl_4$ and 40 mM H_2O_2 for 5 min.



Scheme 1. Electroless plating process with metal colloid used as a catalyst.

Results and Discussion :

We found that hydrogen peroxide reduced the chloroauric acid with the catalytic ability of the Pt nanoparticles. The reduction reaction of the gold ions is believed to progress with the catalysis of the Pt nanoparticles immobilized on a base material as the following chemical equation :

$$2HAuCl_4 + 3H_2O_2 \xrightarrow{Pt} 2Au + 3O_2 + 8HCl \qquad (2)$$

This reaction also takes place with Pd and Au colloids, but the Pt exhibited the most efficient activity among the three metal colloids. Figure 1a is a TEM micrograph showing the Pt nanoparticles immobilized on a thin carbon foil, where the Pt nanoparticles with 3 nm are uniformly distributed on the surface. After 10 seconds of the immersion of this film into the Au plating bath, Au particles with the diameter of 10-30 nm are produced on the Pt nanoparticles as shown in Figure 1b. The number of the Au particles increases with the plating time, and finally the surface is fully covered with the Au particles and the continuous film is formed.

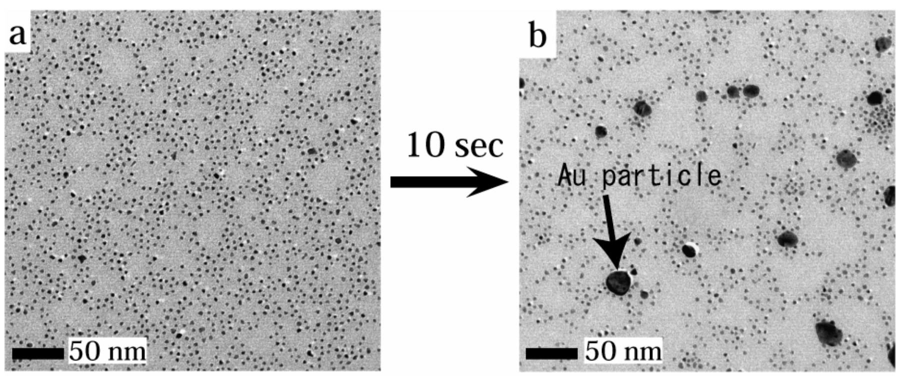


Figure 1. TEM micrographs showing (a) Pt nanoparticles immobilized on carbon thin film and (b) gold particles deposited on the Pt nanoparticles.

This reaction takes place at room temperature and the continuous Au film can be obtained within a few minutes owing to the excellent catalytic property of the Pt nanoparticles. Figure 2a shows the changes in the color of the Kapton® film by the Au plating for 5 min, indicating that the beautiful gold film can be obtained easily. Figure 2b is the plot of the film thickness, estimated from the weight of 4 x 4 cm films, as a function of the plating period at room temperature. The thickness reaches to about 100 nm within 4 min, and then the deposition becomes slow, suggesting that the Pt catalytic surface is almost entirely covered with Au by the catalytic activity of the Pt nanoparticles in the initial 4 min, and afterward, the Au film grows with relatively lower rate by the self-catalytic mechanism.

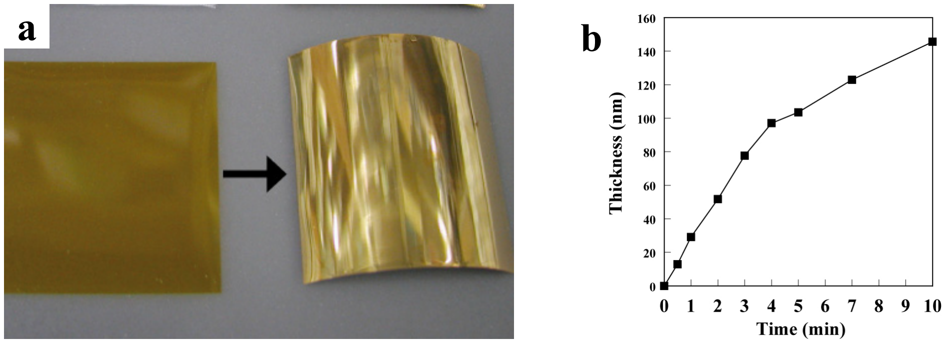


Figure 2. Au electroless plating on Kapton® film (a) and the increase in film thickness with plating time (b).

We found that adhesion of the Au plating film was dramatically enhanced by simple annealing for about 30 minutes at the temperatures ranging from 100°C to 250°C after plating. Thus, strong adhesion of the Au plated films to plastic films can be ensured without using special chemicals or physical surface treatments. As shown in Figure 3, the Au film could not be peeled off the Kapton® film simply by annealing at 240 °C for 5 min. This annealing effect on the adhesion is available for many polymer films. Excellent adhesion could be achieved for polyethylene, polypropylene, polyamide6, polycarbonate and polyphenylene sulfide. The annealed conditions to give high adhesions depend on the properties of polymers: for crystalline polymers, the annealed temperatures should be a little lower than their melting temperatures, while for amorphous polymers, those should be a little lower than their glass transition temperatures.

Figure (3) : Scotch tape test for the evaluation of adhesion of Au film to Kapton® film before and after the thermal annealing at 240 °C for 2 min.

The mechanism for the high adhesion is now under investigation. A TEM micrograph of the cross section of the film (Figure 4) shows that the Pt nanoparticles and the polymer penetrate into the narrow bumps of the Au film at the interface, which may offer the strong physical bonding between the Au and a polymer films.

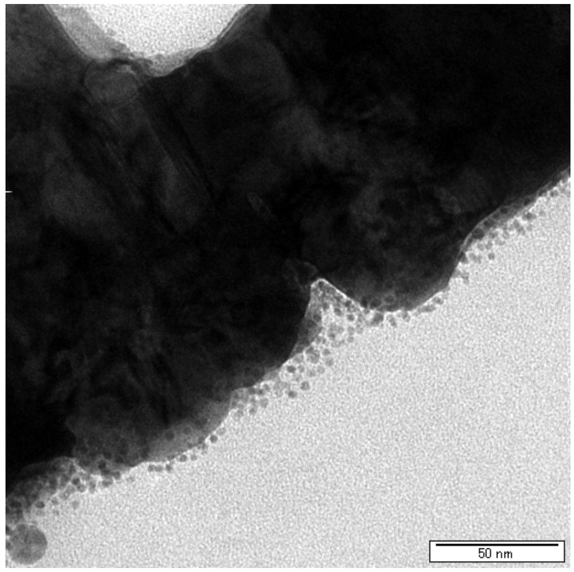


Figure 4. TEM micrograph showing the interface between the Au plated film and Kapton after thermal annealing.

Conclusion :

We have developed novel cyanide-free Au electroless plating using Pt colloid as catalyst. The reaction takes place at room temperature for extremely short time, giving beautiful gold film with tough adhesion to various polymer films. We will extend this technique to electroless deposition techniques for other metals and metal oxides in future.

References :

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