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Electroless Metal Plating on Stearic Acid Layer Spread at Air/water Interface

Hideki MASUDA,* Jia-dan ZHANG, and Nobuyoshi BABA
Department of Applied Chemistry, Faculty of Technology,
Tokyo Metropolitan University, Minamiosawa 1-1, Hachioji, Tokyo 192-03

A thin metal Ag film was obtained at an air/solution interface by using a spread stearic acid layer as a supporting substrate of electroless plating. The properties of the film and the condition of the electroless plating of Ag was examined with scanning electron microscopy and in situ reflectance spectroscopy.

Monomolecular layers of amphipatic molecules have been widely studied for the purpose of fabrication of functional thin films.1) Langmuir-Blogjett (LB) techniques, in which the ordered monolayer of amphipatic molecules was deposited on solid substrates, was commonly used for preparation of functional films.2) The monomolecular films spread at the air/water interface have also attracted much interests from a technological and fundamental viewpoint.3)

In the present report, we demonstrate the preliminary observation of thin metal film formation at the air/water interface using a stearic acid layer as a supporting substrate.4) When the stearic acid layer was spread on the solution which contains Ag salt and a reducing agent, uniform thin metal Ag film was formed at the air/water interface. Without spread of the long chain fatty acid layer, only dispersed fine grain particles of Ag was observed at the interface. Here, the fabrication procedure of the thin metal film and the properties of the deposited metal films examined by scanning electron microscopy were shown.

Stearic acid (Kanto Chemical) was used as a surface active regent. Figure 1 gives a schematic diagram of an experimental set up. The rectangular trough (inside 20 x 300 x 20 mm^3) was fabricated with Teflon. The thin glass plate was used as a floating partition, which was treated with vapor of 1,1,1,3,3,3 hexamethyldisilazane to form a hydrophobic surface. The stearic acid solution (0.1 wt%) was spread on the surface of the solution with a syringe using benzen as a spreading solvent. The surface pressure of the stearic acid was kept constant by use of a piston oil. Oleic acid (Kanto Chemical) was used as the piston oil to generate the constant surface pressure (29.5 dyn cm^{-1}).5)

The solution, on which the stearic acid was spread, was aqueous solution of 3×10^{-2} M $AgNO_3$ with 8×10^{-2} NH_4OH, and 10^{-1} M $C_4H_4KNaO_6$ as a reducing agent. This composition of the solution is similar to that reported by S. K. Guputa for electroless plating bath of Ag.6) Both solutions of the Ag salt with NH_4OH and the reducing agent were prepared in advance separately. After mixing, the solution was put into the trough immediately, and the surface of the solution was cleaned up by sweeping process with clean glass plates. The stearic acid solution was spread at the surface of the solution, and then the stearic acid layer was pressed with a piston oil using the floating glass plate as a partition.

The metal formation at the air/solution interface was analyzed in situ with reflectance spectroscopic measurement. The spectra were recorded with a spectrophotometer equipped with a multichannel analyzer (Otsuka Electronic MCPD-1000). The metal films were observed with a scanning microscope (JOEL J-2000).

Figures 2(a)-(d) show the photographs of the surface of the solution in the course of the Ag deposition. At early stage of the deposition, an optically transparent thin Ag film was observed at the surface (Fig. 2b). The Ag film became thicker with time (Fig. 2c), and the Ag film of the mirror surface was formed after 90 min (Fig. 2d). The thickness of the Ag film deposited over-

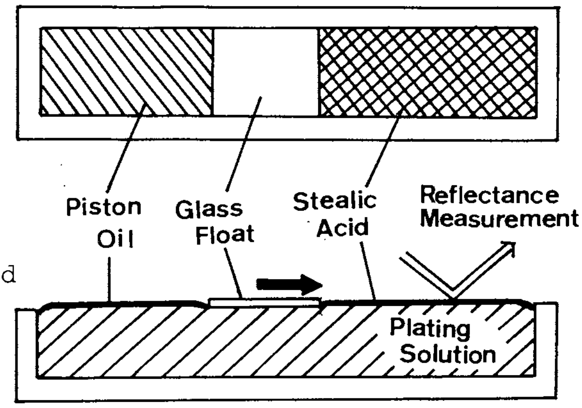

Fig.1. Schematic diagram of experimental set up for electroless plating.

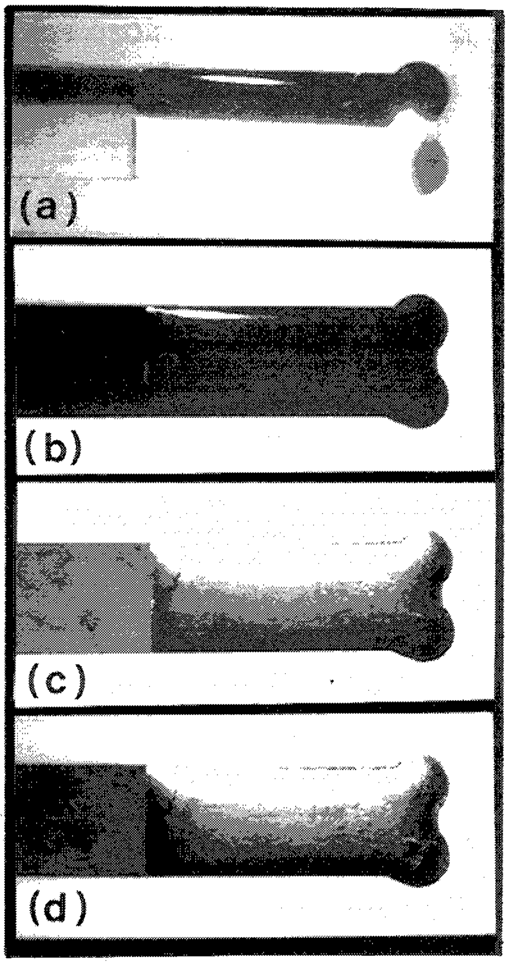

Fig.2. Photographs of change in air/solution interface, 1 min (a), 10 min (b), 60 min (c), 90 min (d).

night was ca. 0.7 μm. This Ag film could be handled with a tweezers. In the case that no stearic acid was presented, the uniform metal film could not formed at the surface but dispersed small particles of Ag was observed.

Figure 3 shows the scanning electron micrographs of the Ag film. The surface of the Ag film in contact with the stearic acid was smooth and flat having fine-grained Ag crystal less than 0.1 μm (Fig. 3a). On the other hand, the surface of the rear side, which was in contact with solution, showed a coarse-grained surface of Ag. This coarse-grained texture can be considered due to the crystal growth of Ag during the deposition, and is in good agreement with the general appearance of the surface obtained by the electro- or electroless plating of Ag.$^{7-9)}$ The results in Fig. 3 a, b implies that the flatness and the texture of the deposited metal films can be controlled by using the smooth surface of the amphipatic molecule layer as a supporting substrate.

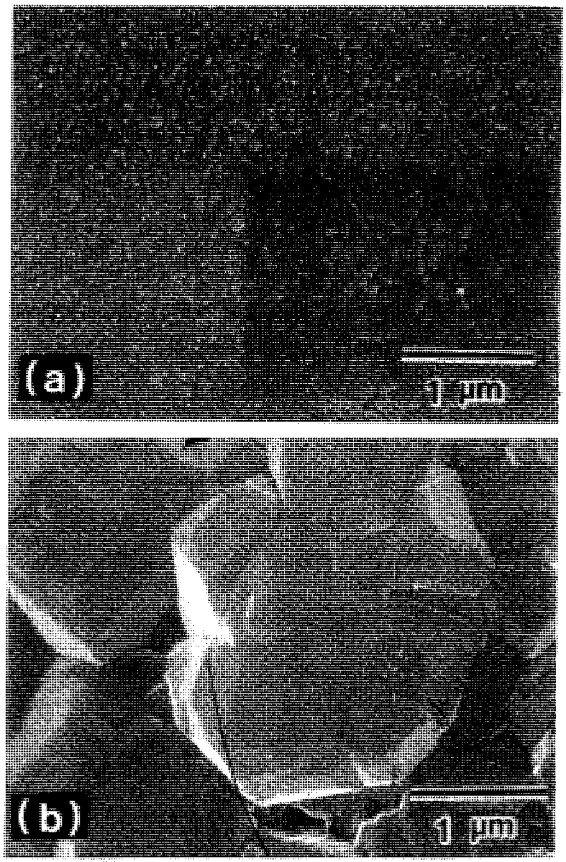

Fig.3. Photographs of Ag film by SEM; surface in contact with stealic acid (a), in contact with solution (b).

Figure 4 shows the results of the in situ reflectance measurement of the air/solution interface. Increase of the reflectance could be observed with time and the spectra obtained were in accord with that of Ag. This indicates that the Ag film with high reflectivity was formed on the stealic acid layer at the interface. On the other hand, only little change in the reflectance at the interface could be observed in the absence of the stearic acid layer. The detailed measurement concerning their optical properties is now in progress.

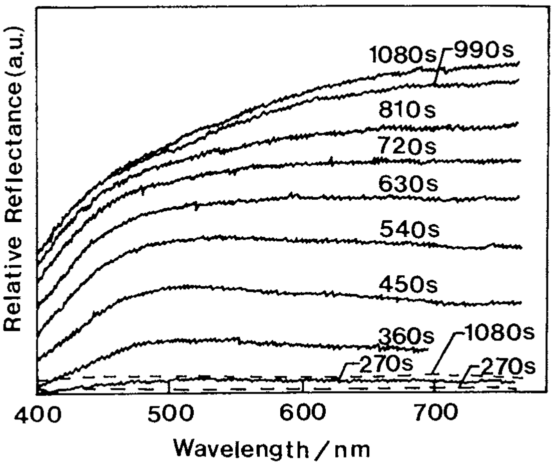

Fig.4. Change in reflectance .a air/solution interface; with (——) and without stearic acid layer (---).

In the case that the oleic acid was

spread on the surface, no Ag deposition could be observed. This dependence of the deposition rate on the type of fatty acids is considered to be due to the difference in the affinity for Ag or the rigidity of the films. However, further examination is required to give a full account of the difference. Applying this dependence of the deposition rate and the properties on long chain fatty acids, one can control the deposition rate and morphology of the Ag film by selecting the ratio of the concentration of the two long chain fatty acids in the spread layer.

The detailed properties of the stearic acid layer at the air/solution interface and the mechanism of Ag deposition is not clear at the present stage. The observed area per molecule at the electroless plating solution measured at the pressure of 29.5 dyn cm^{-1} was reduced to 25%-45% of that at air/distilled water interface. This suggests that the stearic acid dissolved partially into the solution as a micelle and the dissolved stearic acid is in equilibrium with a spread film. From the experimental result, it was shown that the Ag deposition took place only at the spread stearic acid layer.

In conclusion, the formation of the thin Ag film was observed at the air/solution interface by using the spread stearic acid layer. In this method, very thin metal films supported stably on aqueous solution can be obtained. This film can be used by being transferred to the solid substrate. In addition, this metal deposition technique is applicable to the preparation of an in situ replica of the amphipatic molecules layer at the air/solution interface for electron microscopic examination.

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