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Photoreductive Deposition of Palladium for Electroless Copper Plating

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Selective seeding of palladium catalysts on an alumina plate for electroless copper plating was made by photoirradiation. The adsorbed Pd(II)-tartrate were selectively converted to Pd(0) by photoirradiation and the photogenerated Pd(0) catalyzed the electroless copper plating.

Electroless copper plating has been widely applied to printed circuit board manufacturing. The plating is usually initiated with the catalyst based on Pd-Sn colloids.[1,2] For defining the plating circuit polymeric resist is commonly utilized. In aiming at a resist-free process, we have investigated palladium deposition by photoirradiation, and found that Pd(II)-tartrate complexes on an alumina plate are selectively converted to Pd(0) by photoirradiation and the photogenerated Pd(0) particles catalyze electroless copper plating.

Although several processes have been reported to attain selective seeding of catalysts by photoirradiation,[3-8] they have not been used in practical manufacturing. The main reasons are that they require the coating processes of pre-catalyst materials, the exposure process in a vacuum chamber or in solutions, and/or photosensitive substrates. Our method does not require neither the coating processes nor photosensitive

substrates. Further, the process is practical, because tartrate-Pd(II) complexes in aqueous solution are stable to sunlight.

The 30 mm square plates of 96% highgrade alumina(Al_2O_3) were immersed for 10 min in aqueous solutions containing $PdCl_2$ and complexing ligands for Pd(II) and then in deionized water for 3 min, then dried at room temperature. The ligands used in the experiments are as follows; malic acid, citric acid, tartaric acid, ethylendiaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and 2,6-dihydroxybenzoic acid. The pH at the baths was adjusted to 9.3 by the addition of aqueous NaOH. The irradiation was carried out in air under dry conditions typically for 6 min with a high pressure mercury lamp (USHIO USH-500D) radiating through the Toshiba UV-25 filter at a distance of 50 cm. The irradiated plates were dipped in 10% HCl aqueous solution at 60 °C for 5 min to eliminate adsorbed Pd(II)-complexes, rinsed in deionized water, and then immersed in electroless copper solutions for 10 min. The copper plating was carried out in the electroless copper solution containing $CuSO_4$(0.03 mol dm^{-3}), EDTA(0.06 mol dm^{-3}), and formaldehyde(0.1 mol dm^{-3}).

Table 1. Electroless nickel plating on Pd(II)-complexes adsorbed plate[a)]

Ligand [b)]	Before dipping in aqueous HCl	After dipping in aqueous HCl
Malic acid	plating	no-plating
Citric acid	plating	no-plating
Tartaric acid	plating	no-plating
EDTA	no-plating	no-plating
NTA	no-plating	no-plating
2,6-Dihydroxybenzoic acid	plating	no-plating

a) pH=7.5, Temp=60 °C. b) Pd(II)=0.002 mol dm^{-3}, L=0.01 mol dm^{-3}, pH=9.3, Temp=25 °C.

First we examined the adsorption of Pd(II)-complexes on the alumina plate. The adsorption is followed by observing electroless nickel plating, because Pd(II) catalyzes the plating.[9] Table 1 shows the results. Pd(II)-complexes with malic acid, citric acid, tartaric acid, and 2,6-dihydroxybenzoic acid as the ligands are adsorbed on the alumina plate. The adsorbed Pd(II)-complexes were completely eliminated by dipping in HCl aqueous solution at 60 °C.

The adsorbed Pd(II)-complexes did not initiate electroless copper plating. However, the plate adsorbed with Pd(II)-malate, citrate, and tartrate initiated electroless copper plating by photoirradiation. Pd(II)-2,6-dihydroxybenzoic acid was not effective to catalyze electroless copper plating even after photoirradiation. These results indicate that the adsorbed Pd(II) complexes with malate, citrate, and tartrate complexes are photoreduced to Pd(0) by photoirradiation. The wavelength dependence suggested that ligand to metal charge transition (LMCT)[10] is responsible for the photoreduction. Photoirradiation of the Pd(II) complexes in solution did not induce the reductions of the complexes to Pd(0). The UV spectra of the Pd(II)-complex solutions remained

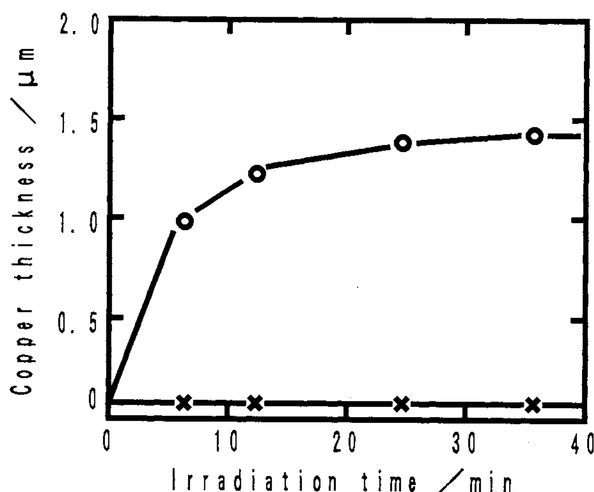

Fig. 1. Plating thickness dependences on irradiation time. (o)tartrate, (x)2,6-dihydroxybenzoic acid were used as the ligands. Plating solution; $CuSO_4$=0.03 mol dm^{-3},EDTA=0.06 mol dm^{-3},HCHO=0.1 mol dm^{-3}, pH=12.7, Plating time=10 min, Temp=60 °C.

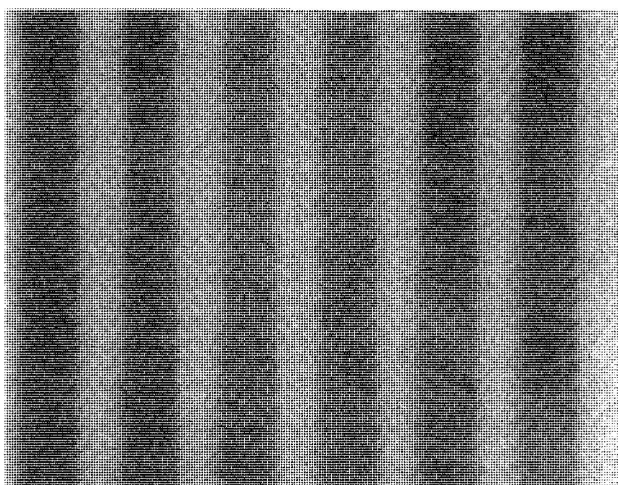

Fig. 2. Optical micrograph of a copper-plated. Vertical copper lines are 200 μm in width.

unchanged by photoirradiation.

Figure 1 shows the dependence of electroless plated copper thickness on irradiation times for Pd(II)-tartrate and Pd(II)-2,6-dihydroxybenzoic acid. Pd(II)-2,6-dihydroxybenzoic acid does not catalyze the plating even after 36 min irradiation, although Pd(II)-tartrate catalyzes electroless copper plating after only 6 min irradiation. The amount of photoreduction depends on the kind of ligands for Pd(II) and adsorption is indispensable for the reaction. Figure 2 shows the copper-plated pattern on an alumina plate. Similar patterns can be produced on glass-epoxy substrates also. The copper plating on these substrates has sufficient adhesion for practical use.

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