Synergistic Effect of Organic Additives and Pulse-Current Plating in a Gold Electrodeposition Acid Bath and Gold Plating Film Corrosion Resistance

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酸系電析金めっき浴での有機添加物および
パルスめっき法の相乗効果とその金めっき膜の耐食性

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Introduction

Gold plating films (0.05 to 0.75 μm) used in electronic parts such as connectors have been made as thin as possible to keep costs as low as possible¹⁾, but the thinner the film, the lower its corrosion resistance due to the increased number of pinholes. Much work has gone into finding ways to raise corrosion resistance^{2)~12)}, including our previous reports on effective polymer additives in baths and efficient film sealing agents^{11), 12)}. To find more effective citric acid baths for gold electrodeposition, we prepared baths containing organic additives such as pyridine derivatives and electrodeposited gold in these baths by pulse-current plating. We then studied the synergistic effect of organic additives and pulse-current plating and evaluated the film's corrosion resistance physicochemically.

Experimental

Materials....Pretreated copper and nickel-electrodeposited brass plates were used as substrates. Gold electrodeposition baths contained potassium dicyanoaurate (I) ($2.9\text{g} \cdot \text{dm}^{-3}$, Au conc. $2.0\text{g} \cdot \text{dm}^{-3}$), citric acid ($100\text{g} \cdot \text{dm}^{-3}$),

cobalt (II) sulfate · heptahydrate ($1.0\text{g} \cdot \text{dm}^{-3}$) and organic pyridine-derived additives such as 2-, 3- and 4-aminopyridine (functional groups : NH_2 ; number of functional group : 1 ; abbrev. : 2, 3 and 4AmPy), pyridine-3-sulfonic acid (SO_3H ; 1 ; 3SulPy), 3-amidopyridine (nicotinamide, CONH_2 ; 1 ; 3AmidPy), 3-thioamido-pyridine (thionicotinamide, COSH ; 1 ; 3ThiPy) and 2, 3-diaminopyridine (NH_2 ; 2 ; 2, 3Am₂Py) (0.01 mol/L). Bath pH was maintained at 3.8.

Electrodepositions....Gold was electrodeposited by direct current (DC, $2.0\text{A} \cdot \text{dm}^{-2}$) and pulsecurrent (PC, average current density $2.0\text{A} \cdot \text{dm}^{-2}$, duty cycle 5 %) at 40°C and 1 atm with stirring. Films were about $0.3\mu\text{m}$ thick.

Measurements....Relative film porosity was evaluated by potentiostatically electrolytic analysis (5 % sulfuric acid, $+0.4\text{V}$ vs. SCE)¹²⁾. A nitric acid (HNO_3) exposure test was also done (conc. HNO_3 , 30°C , 30min), and the ratio of corroded area (%) was determined by ASTM D601-85 standard patterns. Gravimetry determined deposition efficiency¹³⁾. The surface and roughness of the plated film and its roughness were measured using laser microscopy and atomic force microscopy (AFM ; Digital Instruments, Nanoscope-III).

Results and Discussion

Gold plating film prepared without additives by DC (blank/DC) had many pinholes about $0.5\mu\text{m}$ in diameter. That electrodeposited without additives by PC (blank/PC) has fewer pinholes than blank/DC, and that deposited with additives by PC had significantly fewer pinholes.

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Fig. 1 Relationship between relative porosity and concentration of additives.

○ 2AmPy, ● 3AmPy, ● 4AmPy, △ 3ThiPy
△ 3AmidPy, ▲ 3SulPy, □ 2,3Am₂Py

Except for 3 AmidPy, films electrodeposited with additives, were not discolored. Baths with 3 AmidPy produced blue plating film.

The porosity of plating film in blank/PC decreased compared to that in blank/DC (relative porosity (%): blank/PC 100 < blank/DC 611). In the relationship between the concentration of additive and film porosity by PC (**Fig. 1**), porosity decreased with increased additives, particularly when slight amounts of 3ThiPy, 2,3 Am₂Py, and 3AmPy were added. In the HNO₃ exposure test, the corrosion area ratio after electrodeposition by PC increased in the sequence 3ThiPy/PC < 3SulPy/PC < additive-free/PC < additive-free/DC. The corrosion area ratio corresponded to that of porosity.

Deposition efficiency was slightly less with PC than with DC (deposition efficiency (mg/A·min): PC 10 < DC 12.5). In the relationship of deposition efficiency to additive concentration with PC (**Fig. 2**), deposition efficiency decreased with increased concentration except for 2AmPy and 4AmPy, where porosity scarcely decreased. Only 2,3Am₂Py produced both lower film porosity and higher gold deposition efficiency.

AFM showed film surfaces prepared with additives other than 2AmPy and 4AmPy to be microscopically even and clean compared to those blank/DC and blank/PC. To quantitatively evaluate surface roughness, the center line average height (H_{cla}) of film was determined by statistically analyzing AFM images. H_{cla} values of films prepared in baths with additives were smaller than in blank/DC and blank/PC (H_{cla} (nm): 3ThiPy/PC 3.9, 2,3Am₂Py/PC 5.0, 3SulPy/PC 5.8, 3AmidPy/PC 6.1, 3AmPy/PC 6.9, blank/PC 7.7 and blank/DC 9.1)

Fig. 2 Relationship between deposition efficiency and concentration of additives.

○ 2AmPy, ● 3AmPy, ● 4AmPy, △ 3ThiPy
△ 3AmidPy, ▲ 3SulPy, □ 2,3Am₂Py

Thus, using both additives such as pyridine derivatives and PC in citric acid bath systems effectively lowered porosity and increased deposition efficiency compared to using DC, additive/DC, and PC. Lower porosity and higher deposition efficiency were particularly obvious, thus confirming the synergistic effect of organic additives and pulse-current plating.

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