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Deposition of Copper Using Photoexcited Riboflavin

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In the presence of riboflavin and ethylenediaminetetraacetic acid (EDTA), deposition of copper was observed upon irradiation. Selective deposition of copper onto irradiated parts of a riboflavin-adsorbed alumina substrate was accomplished in an electroless copper plating solution containing EDTA. Two lines per millimeter were written on the substrate. The peel adhesion strength of the plated copper layer was comparable to that of a copper layer plated by a conventional method.

Noble metals,1) copper,2,3) and nickel4) are photoelectrochemically deposited onto semiconductor particles in the presence of salts of these metal ions and sacrificial reagents. This phenomenon occurs because of electron transfer from the sacrificial reagent in the solution to photogenerated holes in the valence band of the semiconductor particles and from the conduction band of the semi-conductor particles to the metal ions in the solution. Therefore, these two energy bands (one is filled with and another is not filled with electrons) are very important for the photoelectrochemical deposition of metals.

In the case of organic compounds, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are expected to act like the valence band and the conduction band, respectively, of semi-conductor materials. The photoexcited electrons in the LUMO of organic compounds, i.e. dyes, have attracted much interest in the study of electron transfer to semi-conductor materials including silver halides (the photo-sensitizing effect)5,6) and to metal electrodes (the photo-galvanic effect).7—9) Especially in some photo-galvanic studies, the potential of an irradiated electrode in the solution is negative enough to deposit metals from the solution containing salts of the metal ions. However, few studies have been done concerning the deposition of metals using photoexcited organic compounds. Focusing on typical dyes employed in studies of the photo-sensitizing and photo-galvanic effects, we studied the possibility of the deposition of copper with irradiation, and found that the photoelectrochemical deposition of copper occurs when riboflavin or another kind of dye is used.

This paper reports on the phenomenon and the mechanism of the deposition of copper using photoexcited riboflavin. The resolution and peel adhesion strength of the plated copper layers on a riboflavin-adsorbed alumina substrate are also described.

Experimental

Materials and Experimental Apparatus. Riboflavin was used as the organic dye; its concentration was 10^{-5} M (1 M=1 mol dm^{-3}). EDTA at a concentration of 1—2×10^{-2} M was used as the sacrificial reagent. Copper(II) sulfate pentahydrate ($CuSO_4\cdot5H_2O$) was used at a concentration of 0.01 M. All reagents were purchased from Wako Pure Chemical Industries, Ltd. Riboflavin was a first grade reagent, and the others were special grade reagents. The pH value of the solution was adjusted to be between 5 and 12.3 by adding conc sulfuric acid or sodium hydroxide aqueous solutions.

A 250 W super-high-pressure mercury lamp was used as a light source. The light was applied through an IR-cutting filter to the solutions in a test tube for 10—120 min. The oxygen concentration in the solution was measured by a dissolved oxygen meter (Central Kagaku, UC-12). All of the experiments were carried out under an air atmosphere.

Plating on an Alumina Plate. Degreased 96% alumina substrates (Kyocera) were etched in a 2.5 M hydrofluoric acid solution, and rinsed with ion-exchanged water. The alumina substrates were then immersed in a 1 M sodium hydroxide solution for 1 h, and rinsed thoroughly with ion-exchanged water. After drying at 85 °C, the alumina substrates were immersed in a solution containing 5×10^{-5} M riboflavin for 60 h. From the diffuse reflectance spectrum of the riboflavin-adsorbed alumina substrate and the change in the absorbance spectrum of the solution by immersing the alumina substrates, the amount of riboflavin adsorbed onto the alumina substrate was estimated to be ca. 6×10^{-9} mol cm^{-2}.

An electroless copper plating solution consisting of EDTA (0.3 M), copper(II) sulfate (0.04 M), and formaldehyde (0.1 M) was employed. The pH value of the solution was 12.3. The temperature of the solution was ca. 60 °C. The riboflavin-adsorbed alumina substrate was set in the electroless copper plating solution about 1 mm behind a mask (Melles Griot, USAF1951). Light was applied through the mask to the substrate for 30 s. After irradiation, the substrate was kept in the electroless copper plating solution for 20 min. The thickness of the plated copper layers was ca. 2

µm.

Measurement of Peel Adhesion Strength. Using a mask with 4 mm^2 (2 mm×2 mm) windows, copper was plated onto the riboflavin-adsorbed alumina substrate in the electroless copper-plating solution. In order to compare this photo-plating method with a conventional plating method, copper layers with the same shape were electroless-plated onto the alumina substrate with commercially available seeding solutions (Shipley, Cataprep 404, Cataposit 44, and Accelerator 19) and a screen printing technique. The thickness of the plated copper layers was ca. 12 µm in both cases. To avoid the formation of intermetallic compounds with the plated copper and solder, nickel was plated onto the copper layers by using a commercially available electroless nickel-plating solution (Nippon Kanigen, S754-1, S754-2). The thickness of the nickel layers was ca. 1 µm. A tin-plated copper wire of 0.8 mm diameter was laid on the nickel layer and then soldered. One terminal of the copper wire was connected to a tensile tester (Seishin Trading, SS-15KP), and the peel adhesion strength of the plated copper layer was measured.

Results and Discussion

Deposition of Copper. In all the test solutions with riboflavin, yellowish or blackish-brown deposits were observed upon irradiation. After filtration of the solutions, the residue on the filter paper was identified by X-ray diffraction. The results are shown in Table 1. The deposits were identified to be copper(I) oxide (Cu_2O) and/or copper metal (except pH=9). On the other hand, no deposit was observed even after irradiation for 2 h in the same series of experiments without riboflavin.

In order to clarify these phenomena, the residue on the filter paper was dissolved in a conc nitric acid solution and the amount of reduced Cu^{2+}–EDTA complex was analyzed with ICP-AES. The change in the oxygen concentration in the solution was also measured as a function of irradiation time. The results are summarized in Fig. 1. Since Cu^{2+} ion and EDTA form a stable Cu^{2+}–EDTA complex,$^{10)}$ free EDTA (that was not used for forming the Cu^{2+}–EDTA complex) is important in classifying the results as follows:

1) In the solution containing only riboflavin, the decrease in the oxygen concentration appeared to be slight.

2) In the presence of riboflavin and free EDTA, the oxygen concentration in the solution rapidly decreased to 0 upon irradiation.

3) In the case of the solution containing riboflavin, the Cu^{2+}–EDTA complex, and free EDTA, reduction of the Cu^{2+}–EDTA complex was observed just after the oxygen concentration reached 0. After irradiation for 2 h, the amount of reduced Cu^{2+}–EDTA complex

Table 1. Type of Deposits

pH	Irradiation time/min	
	10	120
12.3	Cu_2O	Cu_2O, Cu
11	—$^{a)}$	Cu_2O, Cu
9	—	—
7	—	Cu
5	—	Cu

a) —denotes the deposit showed halo X-ray diffraction pattern.

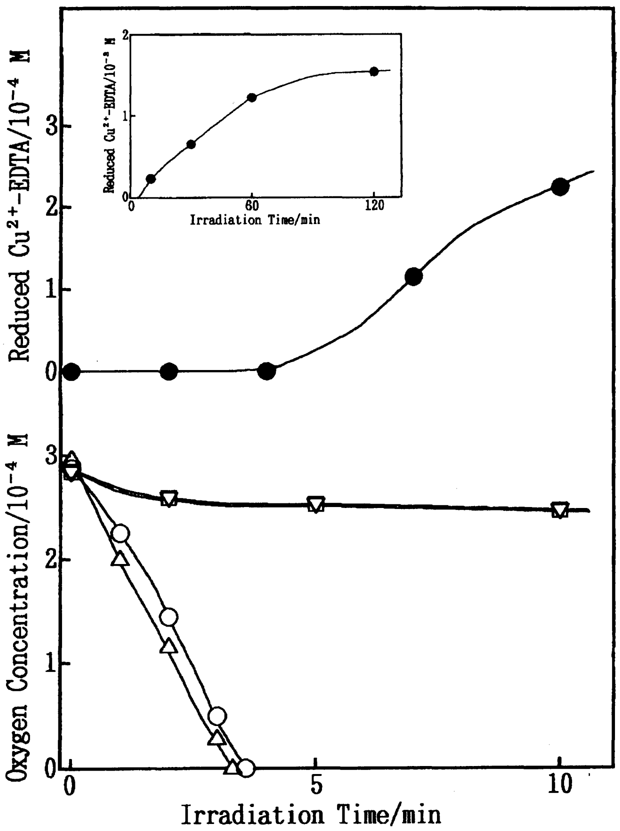

Fig. 1. Oxygen concentration and the amount of reduced Cu^{2+}–EDTA vs. irradiation time: (▽) riboflavin of 10^{-5} M; (△) riboflavin of 10^{-5} M + EDTA of 2×10^{-2} M; (○, ●) riboflavin of 10^{-5} M + EDTA of 2×10^{-2} M + $CuSO_4\cdot5H_2O$ of 1×10^{-2} M; (□) riboflavin of 10^{-5} M + EDTA of 1×10^{-2} M + $CuSO_4\cdot5H_2O$ of 1×10^{-2} M. Inset: the amount of reduced Cu^{2+}–EDTA vs. irradiation time.

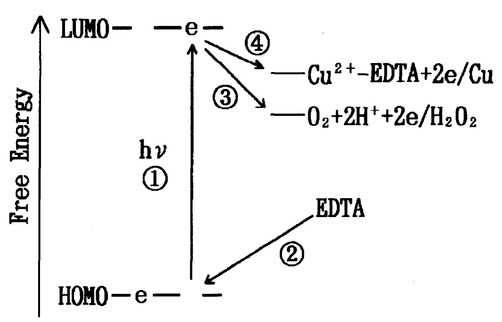

Fig. 2. Schematic energy diagram for the photoelectrochemical reduction of copper by riboflavin (Rib.) and EDTA.

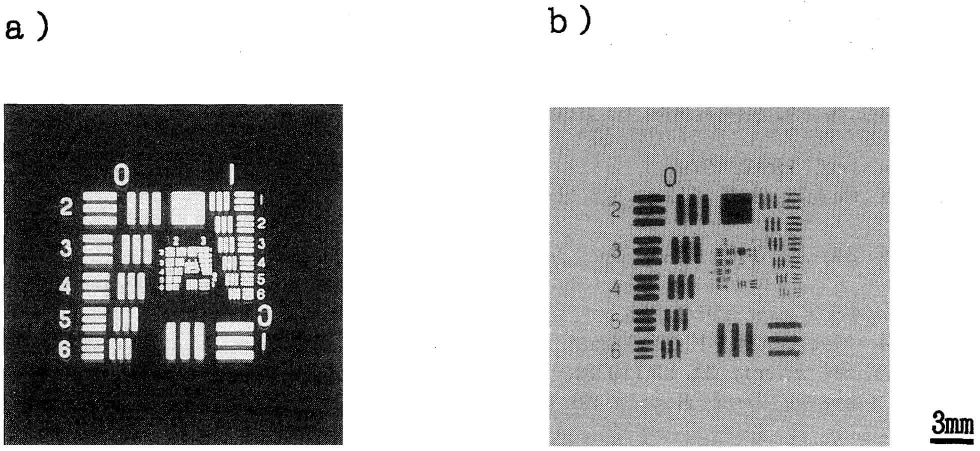

Fig. 3. (a) the mask. (b) pattern of deposited copper on the alumina substrate.

was more than 1.5×10^{-3} M. This value was about 150 times as large as the concentration of riboflavin.

4) However, in the solution containing riboflavin and the Cu^{2+}–EDTA complex without free EDTA, the decrease in the oxygen concentration appeared to be slight, and reduction of the Cu^{2+}–EDTA complex was not observed.

From these results and the mechanism of the photogalvanic effect on the riboflavin–EDTA system,[11—13] the reduction mechanism of the Cu^{2+}–EDTA complex upon irradiation is thought to be as shown in Fig. 2. Riboflavin absorbs light and produces a photoexcited electron in the LUMO and an electron-vacancy (hole) in the HOMO (①). An electron from free EDTA flows to the hole in the HOMO (②). A photoexcited electron in the LUMO flows to oxygen in the solution (③), and riboflavin is regenerated. Thus, the oxygen concentration in the solution decreases to 0 in a few minutes. Under these conditions, a photoexcited electron in the LUMO then reduces the Cu^{2+}–EDTA complex to Cu_2O or copper metal (④).

It is well-known that many amines adsorb on a metal surface and prevent the metal from corroding.[14] EDTA is thought to act as such an inhibitor for the oxidation of the deposited Cu_2O or copper metal during the filtration and the X-ray diffraction measurements under an air atmosphere.

Copper Pattern on an Alumina Substrate. EDTA is used as a complexing agent for Cu^{2+} ion in an electroless copper plating solution.[15] If the photoelectrochemical deposition of copper occurs on a riboflavin-adsorbed substrate in the electroless copper plating solution, the amount of deposited copper is expected to be enhanced by the electroless copper plating reaction after irradiation.

Figure 3 shows the mask employed and the plated copper pattern on the riboflavin-adsorbed alumina substrate. Judging from the line separation of the pattern, two lines per millimeter could be written on the riboflavin-adsorbed alumina substrate by the photo-plating method.

Peel Adhesion Strength of Plated Copper. Figure 4 shows the relationship between the peel adhesion strength of the plated-copper layers and the etching amount of the alumina substrate. Without etching, copper was not plated on the riboflavin-adsorbed alumina substrate upon irradiation. However, photo-plating of copper was observed when the etching amount was more than 0.1 mg cm^{-2}. In this region, the peel adhesion strength of the photo-plated copper layers was comparable to that plated by the conventional method.

Compared to conventional plating methods for forming printed wiring boards,[16] the photo-plating method has the following characteristics:

1) It does not require any palladium colloids that act as nuclei in an electroless copper-plating reaction.

2) Copper patterns are formed with simple processes without resists.

This method is expected to be more effective for forming copper patterns on three-dimensional (curved or stepped) substrates than the conventional method.

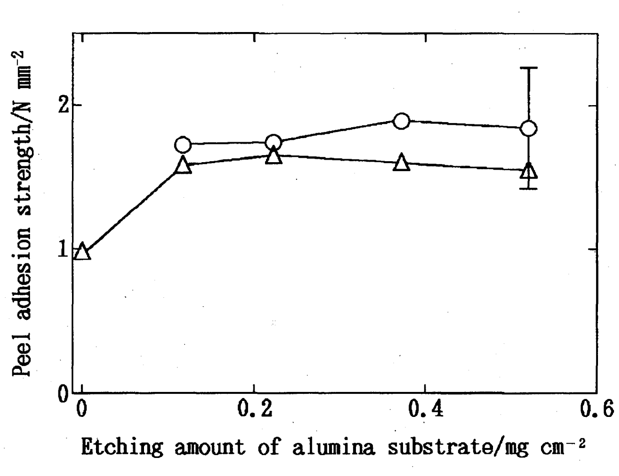

Fig. 4. Peel adhesion strength of the copper layer on the alumina substrate vs. the etching amount of the alumina substrate: (○) plated on a riboflavin-adsorbed alumina substrate; (△) plated on an alumina substrate activated with commercially available seeding solutions.

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