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Photoelectrochemical Deposition of Copper on TiO_2 Particles. Generation of Copper Patterns without Photoresists

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In the presence of EDTA or 2,2',2"-nitrilotriethanol, copper was photoelectrochemically deposited on TiO_2 particles. Selective deposition of copper on irradiated parts of a TiO_2-sol-adhered alumina plate was accomplished in an electroless copper plating solution containing EDTA.

It is reported that similar to the other metals (Pt, Au, Pd, and Ag), Cu deposits on TiO_2 particles with irradiation in the presence of Cu^{2+} ion and sacrificial electron donors such as alcohols or their oxidized products (aldehydes or acids).[1-3] Although ethylenediaminetetraacetic acid (EDTA) and 2,2',2"-nitrilotriethanol (TEA) are known to be typical sacrificial electron donors in photoelectrochemistry, few studies have been reported on the deposition of metals on TiO_2 particles with irradiation in the presence of these sacrificial electron donors. This paper reports the photoelectrochemical deposition of Cu on TiO_2 particles by using EDTA or TEA instead of methanol and acetic acid under the atmosphere.

TiO_2 sol[5)] with a concentration of 1 g dm^{-3} was employed as TiO_2 particles. Copper(II) sulfate ($CuSO_4$)[5)] was also employed, and its concentration was 5×10^{-3} M (1 M = 1 mol dm^{-3}). Methanol,[5)] acetic acid,[5)] EDTA,[5)] and TEA[5)] were employed as sacrificial electron donors. The concentration of methanol and acetic acid was 0.2 M and the concentration of the other sacrificial electron donors was 0.02 M. The pH value of the solution was adjusted to be between 5 and 13 by adding conc. H_2SO_4[5)] or NaOH[5)] aqueous solutions. A 250 W super high pressure mercury lamp (USHIO, USH250D) was employed as a light source. The light was applied through an IR-cutting filter to the solutions in test tubes for 10 minutes. All the experiments were done without outgassing.

Some solutions were changed in color with irradiation, and after the filtration of the solutions, the residue on the filter paper was identified with X-ray diffraction method. The results are summarized in Table 1. In the neutral and alkaline solutions, although Cu^{2+} ion (Cu^{2+}-EDTA or TEA complex) was easily reduced to Cu^+ ion or Cu metal in cases of EDTA and TEA[6], the experiments were not able to be done due to the formation of CuO in cases of methanol and acetic acid. In the solutions (pH=5), in which Cu^{2+} ion was stable without complexing reagents (EDTA and TEA), the deposition of Cu was observed only in the case of EDTA.

In order to clarify these phenomena, the concentrations of oxygen[7] in the solutions (pH=5) and the Cu / Ti molar ratio[8] of the residue on the filter paper were measured as a function of irradiation time as summarized in Fig. 1. In the presence of TiO_2 sol, EDTA, and $CuSO_4$, the oxygen concentration in the solution rapidly decreased to 0 and the deposition of Cu was observed.

Table 1. Type of Deposits on TiO_2 Particles with Irradiation

	sacrificial electron donors			
pH	EDTA	TEA	methanol	acetic acid
13	Cu_2O	Cu	X[b]	X
11	Cu_2O	Cu_2O	X	X
9	Cu	Cu_2O	X	X
7	Cu	Cu_2O	X	X
5	Cu	-[a]	-	-

Cu : Color of the solutions turned black or reddish black due to deposition of Cu.

Cu_2O: Color of the solutions turned blackish yellow due to deposition of Cu_2O.

a) - denotes no changes in color.
b) X denotes CuO was formed when the pH value was adjusted.

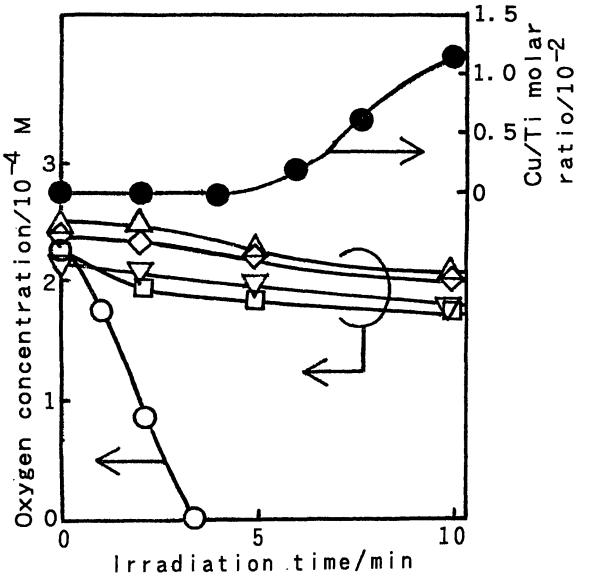

Fig. 1. The concentration of oxygen and the Cu / Ti molar ratio of the residue as a function of irradiation time.

◇	:	0.005 M $CuSO_4$ + 0.02 M EDTA
□	:	1g dm^{-3} TiO_2 + 0.02 M EDTA
○, ●	:	1g dm^{-3} TiO_2 + 0.005 M $CuSO_4$ + 0.02 M EDTA
△	:	1g dm^{-3} TiO_2 + 0.005 M $CuSO_4$ + 0.2 M methanol
▽	:	1g dm^{-3} TiO_2 + 0.005 M $CuSO_4$ + 0.2 M acetic acid

From these results, deposition mechanism of Cu or Cu_2O with irradiation is thought to be as shown in Fig. 2. TiO_2 particles absorb UV light (1) and produce a photoexcited electron in conduction band (c. b.) and a hole in valence band (v. b.). The hole flows to a OH^- ion (2) and produced $OH^\cdot$ radical then oxidizes the sacrificial electron donors (3).[9-11] Since the deposition of Cu or Cu_2O was observed in a large pH region, the electron flow rates in these steps are thought to be sufficiently high. On the other hand, the photoexcited electron flows to an oxygen (4) or a Cu^{2+}-EDTA complex (5), and reduced Cu^{2+}-EDTA complex is then oxidized with the oxygen (6). The two curves (—□— and —○—) in Fig. 1 show that in the presence of the Cu^{2+}-EDTA complex, the oxygen in the solution is rapidly reduced with the photoexcited electron through steps (5) and (6) and the oxygen concentration in the solution decreases to 0 in a few minutes. This condition is also observed in the outgassed solution, and the photoexcited electron reduces the Cu^{2+}-EDTA complex to Cu_2O or Cu in consequence. It is well known that many amines adsorb on a metal surface and prevent the metal from corroding. EDTA and TEA are thought to act as such inhibitors for the oxidation of the deposited Cu_2O or Cu.

EDTA and TEA are also used as complexing reagents for Cu^{2+} ion in electroless copper plating solutions. If photoelectrochemical deposition of Cu occurs on TiO_2 particles in the electroless copper plating solutions, the deposited Cu is thought to act as a nucleus for the electroless copper plating reactions and continuous deposition of Cu occurs even after irradiation.

An electroless copper plating solution containing EDTA of 0.3 M, $CuSO_4$ of 0.04 M, and formaldehyde[5] of 0.1 M was employed. The pH value of the solution was 12.5. A degreased and etched 96% Alumina plate (Kyocera) was immersed in the TiO_2 sol solution of 1 g dm^{-3} and dried at 85℃. The amount of adhered TiO_2 sol is ca. 1×10^{-6} g cm^{-2}. The plate was

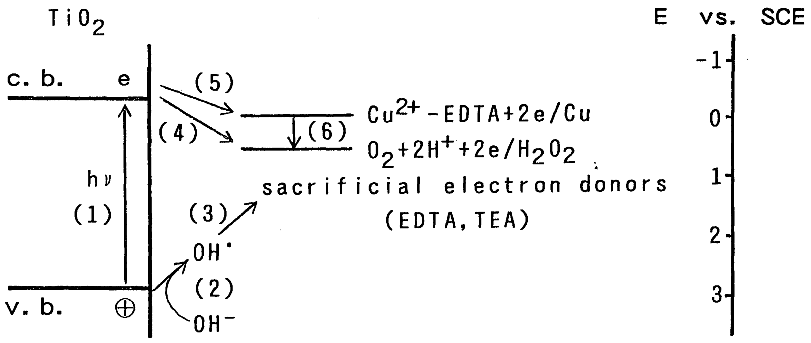

Fig. 2. The schematic diagram for photoelectrochemical deposition of Cu on TiO_2 particles.

set in the electroless copper plating solution about 5 mm behind a mask. The light was applied through the mask to the alumina plate for 5 minutes. After irradiation, the alumina plate was kept in the solution for 60 h. The results are shown in Fig. 3. Deposition of Cu was observed on the irradiated parts of the alumina plate. From the SEM photograph of the fractured Cu layer, the thickness of the Cu layer was observed to be about 60 µm and the selective deposition of Cu patterns without photoresists was accomplished in the electroless copper plating solution containing EDTA.

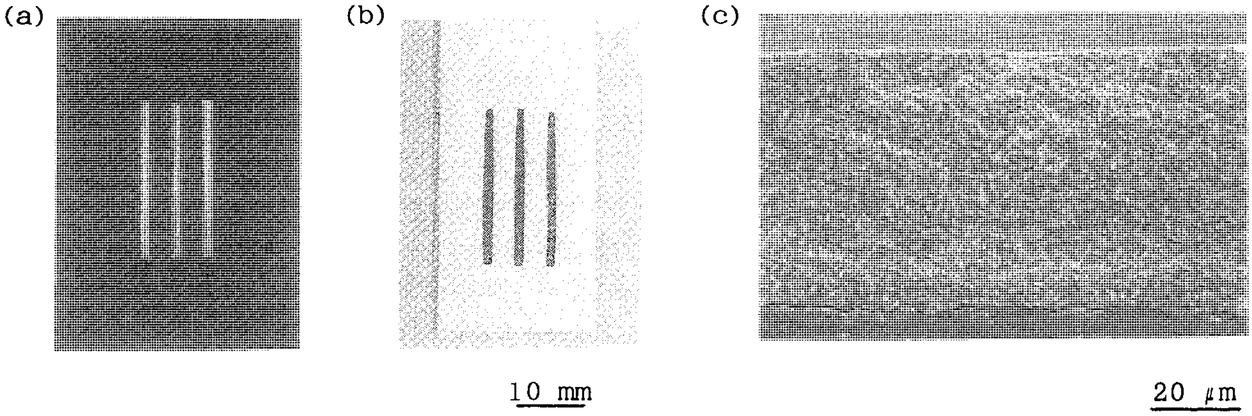

Fig. 3. (a) the mask employed. (b) deposited Cu pattern on the alumina plate. (c) SEM photograph of fractured Cu pattern.

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5) TiO_2 sol was purchased from Nissan Chemical Industries and the others were purchased from Wako Pure Chemicals as guaranteed reagents.
6) Observed d values were 1.80 Å and 2.09 Å in case of Cu and 2.13 Å, 2.47 Å, and 3.02 Å in case of Cu_2O.
7) Measured with a DO meter (Central Kagaku, UC-12).
8) Desolved in a conc. $HF-HCl-HClO_4$ aqueous solution and analyzed with ICP-AES.
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