CHEMISTRY LETTERS, pp. 331-334, 1993.

Effects of Potassium Hexacyanoferrate(II) on Electroless Copper Plating in the Presence of Excess 2,2',2"-Nitrilotriethanol

Koji KONDO,* Katsuaki KOJIMA, Nobumasa ISHIDA, and Masahiro IRIE†
Nippondenso Co., LTD., Production Eng. Dept.,
1-1, Showa-cho, Kariyashi, Aichi 448
†Kyushu University, Institute of Advanced Material Study,
Kasugakoen, 6-1, Kasuga, Fukuoka 816

With the addition of potassium hexacyanoferrate(II) to the 2,2'2"-nitrilotriethanol (TEA) electroless copper bath, the effects of the plating rate and the deposit quality were examined. The required concentration to improve the quality of the TEA bath was 10 times higher than that in the ethylenediaminetetraacetic acid (EDTA) bath.

Electroless copper plating has been progressively improving for the fabrication of printed circuits. The improvements in electroless copper plating are mainly the stability, the deposit quality and the plating rate. The instability of electroless copper baths mainly result from disproportionation of Cu_2O.1) Additives, such as alkali cyanides, 2,2'-bipyridyl, o-phenanthroline and 2-mercaptobenzothiazole, stabilize the electroless copper bath by preventing disproportionation of Cu_2O.1) On the other hand, additives such as 2,2'-bipyridyl,2) potassium cyanonickelate3) and potassium hexacyanoferrate(II)4) are practical for improving deposit quality. In an attempt to increase the rate, the additives,5) the ligands,6) and coordination structures7) have been investigated. Recently, we have found that excess 2,2',2"-nitrilotriethanol (TEA) is effective to increase the electroless copper plating rate8) and that the high plating rate is due to the adsorption of Cu(II)-TEA complex onto the TEA adsorbed surface.[9] 2,2'-bipyridyl and potassium hexacyanoferrate(II) have been utilized for improving the quality and the stability of TEA bath.[8] In this study, we examined the effect of potassium hexacyanoferrate(II) on the deposit quality and the plating rates in the TEA bath.

The solutions were prepared with analytical grade reagents and deionized water. The electroless copper solution contained 0.22 mol dm^{-3} formaldehyde, NaOH, $CuSO_4$, TEA, and potassium hexacyanoferrate(II). The solution pH was adjusted to 12.8 by adding aqueous NaOH. The potassium hexacyanoferrate(II) concentration dependences of the plating rate were measured at various Cu(II) in the presence of excess TEA (0.12-1.0 mol dm^{-3}). The Cu(II) concentrations were varied from 0.01 to 0.06 mol dm^{-3}. The potassium hexacyanoferrate(II) concentrations were varied from 4.7×10^{-5} to 7.1×10^{-4} mol dm^{-3}. After plating for 5 and 10 min at 60 °C, the plated substrates were weighed to determine the copper plating rate. Pretreatments of the substrate and plating procedure are the same as described before.[8] A scanning electron microscope (SEM) was used to observe the surface morphologies.

With the addition of potassium hexacyanoferrate(II) to the ethylenediaminetetraacetic acid (EDTA) bath, the effects of the plating rate and on the surface structure were reported by Veleva.[4] The increase of potassium hexacyanoferrate(II) concentration decreased the plating rate. With the addition of potassium hexacyanoferrate(II) 5.0×10^{-5} mol dm^{-3}, the plating rate decreased by half. The effects were attributed to the presence of free cyanide ions in the bath. The introduction of 5.0×10^{-5} mol dm^{-3} potassium hexacyanoferrate(II) into the EDTA bath abruptly changes the nodular copper surface to the smoother surface.[4]

Figure 1 shows the dependence of plating rate for various Cu(II) on the potassium hexacyanoferrate(II) concentration in the TEA bath. The plating rate was scarcely affected by adding potassium hexacyanoferrate (II) up to 7.1×10^{-4} mol dm^{-3}. The rate decreased to 80% in the presence of 7.1x10^{-4} mol dm^{-3}. At potassium hexacyanoferrate(II) concentration below 2.4x10^{-4} mol dm^{-3} the plating bath decomposed after plating. At the concentration of 7.1x10^{-4} mol dm^{-3} potassium hexacyanoferrate(II) the bath was sufficiently stable.

Figure 2a shows the surface morphology of deposit obtained from the TEA bath containing 5.0x10^{-5} mol dm^{-3} potassium hexacyanoferrate(II). The

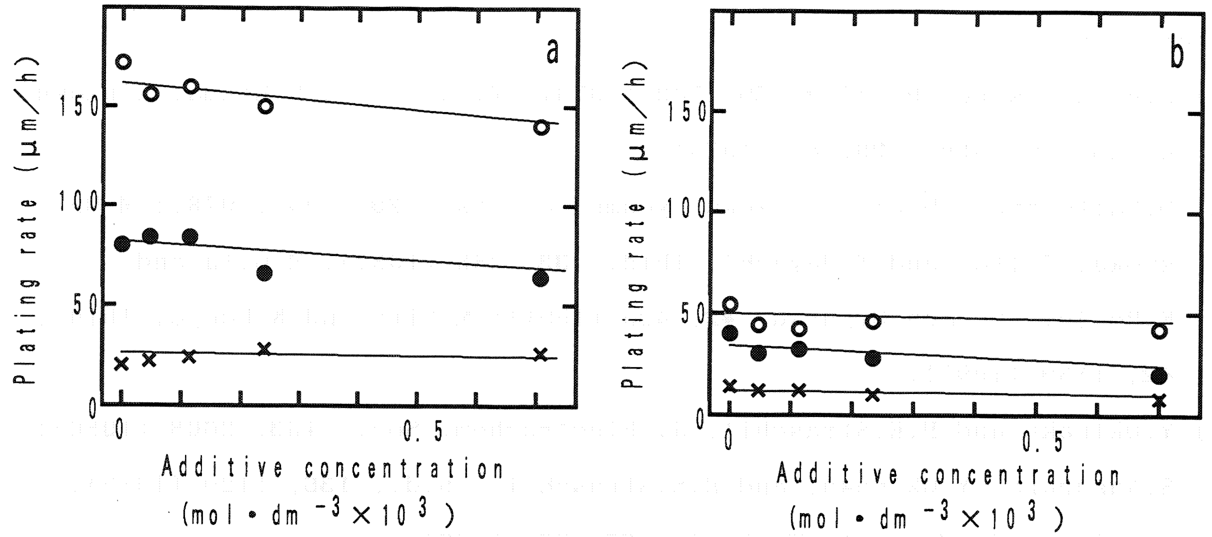

Fig. 1. Effects of potassium hexacyanoferrate(II) on the plating rate for various excess TEA concentrations; **(a)**1.2x10^{-1}mol dm^{-3}; **(b)**1.0mol dm^{-3}; and for various Cu(II) concentrations: (○)6.0x10^{-2}mol dm^{-3}; (●)3.0x10^{-2}mol dm^{-3};(×)1.0x10^{-2}mol dm^{-3}.

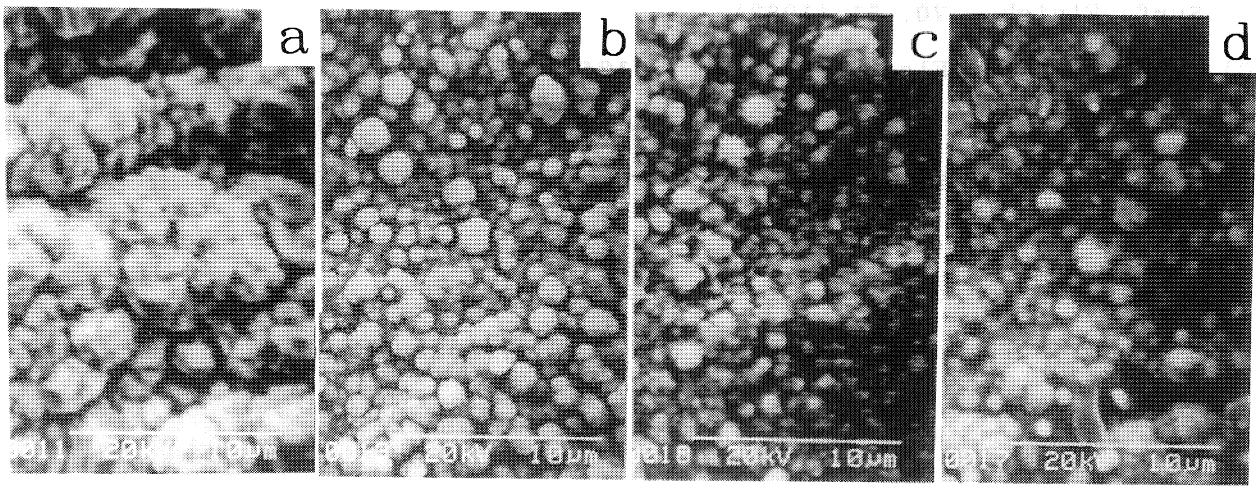

Fig. 2. Surface morphologies of TEA electroless copper deposited in the presence of the following potassium hexacyanoferrate(II) concentrations: **(a)**5.0x10^{-5}mol dm^{-3}; **(b)**2.4x10^{-4}mol dm^{-3}; **(c)**4.7x10^{-4}mol dm^{-3}; **(d)**7.1x10^{-4}mol dm^{-3}. Plating time: 10 min.

surface was very porous in comparison with the surface obtained from EDTA bath. The effect of potassium hexacyanoferrate(II) on the surface morphology was examined, as shown in Fig.2. As can be seen from the figure, the concentration above 4.7×10^{-4} mol dm^{-3} was required to improve the deposit surface. In the plating process, the differences in the effects between EDTA and TEA baths suggested that the role of potassium hexacyanoferrate(II) in the TEA bath is distinct from that in the EDTA bath.

References

1) E.B.Saubestre, Plating, **59**, 563 (1973); M.Saito and H.Honma, Kinzoku Hyoumen Gijutsu, **29**, 88 (1978).
2) M.Saito and H.Honma, Kinzoku Hyoumen Gijutsu, **29**, 190 (1978); M.Matsuoka, S.Ito, and T.Hayashi, ibid., **33**, 385 (1982); M.Oita and K.Honjo, Hyoumen Gijutsu, **42**, 425 (1991); M.Oita and K.Honjo, ibid., **42**, 1169 (1991).
3) Y.Okinaka and H.K.Straschil, J. Electrochem. Soc., **133**, 2608 (1986); S.Nakahara, Y.Okinaka, and H.K.Straschil, ibid., **136**, 1120 (1989).
4) R.Veleva, Surf. Coat. Technol., **29**, 87 (1986).
5) L.N.Schoenberg, J. Electrochem. Soc., **119**, 1491 (1972); A.Hung, ibid., **132**, 1047 (1985); A.Hung, ibid., **133**, 1350 (1986); F.J.Nuzzi, Plat. Surf. Finish., **70**, 51 (1983).
6) M.Paunovic, J. Electrochem. Soc., **124**, 349 (1977).
7) L.N.Schoenberg, J. Electrochem. Soc., **118**, 1571 (1971).
8) K.Kondo, J.Ishikawa, O.Takenaka, T.Matsubara, and M.Irie, J. Electrochem. Soc., **137**, 1859 (1990); K.Kondo, J.Ishikawa, O.Takenaka, T.Matsubara, and M.Irie, ibid., **138**, 3629 (1991).
9) K.Kondo, N.Ishida, J.Ishikawa, and M.Irie, Bull. Chem. Soc. Jpn., **65**, 1313 (1992).

(Received November 12, 1992)