Synergistic Effects of 2,2′-Bipyridyl and Potassium Hexacyanoferrate(II) on Electroless Copper Plating from Triethanolamine Bath

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

(Received February 15, 1993)

The synergistic effects of 2,2′-bipyridyl and potassium hexacyanoferrate(II) on the plating rate and the deposit quality were examined in the triethanolamine (TEA) electroless copper bath. The simultaneous addition of 2,2′-bipyridyl and potassium hexacyanoferrate(II) enhanced not only the plating rate but also the foil quality. The elongation of the foil produced in the TEA bath containing these two additives was 10 times larger than that produced in the bath containing only 2,2′-bipyridyl. The analysis based on the adsorption model revealed that the simultaneous addition of 2,2′-bipyridyl and potassium hexacyanoferrate(II) increases the respective adsorption equilibrium constants. From the analysis, the synergistic effects was attributed to the adsorption of 2,2′-bipyridyl and potassium hexacyanoferrate(II) on the surface with mutual interactions.

Electroless copper plating process has recently attracted much attention because of its use in the manufacture of printed circuits and its potential application to many other electronic devices. Although the process makes it possible to plate directly on nonmetallic substrates, the serious drawback of the plating is the low plating rate. In an attempt to accelerate the rate the additives,[1)] the ligands,[2)] and the coordination structures[3)] have been investigated. Recently, we have found that excess triethanolamine (TEA) is effective to accelerate the rate[4,5)] and that the plating rate was over 20 times faster than the rate in the current ethylenediaminetetraacetic acid (EDTA) bath. We demonstrated that the high plating rate is due to the adsorption of TEA–Cu(II) complex onto the TEA adsorbed surface.[6)]

The TEA bath requires some additives to prevent bath decomposition and to improve the copper foil. The foil quality in the absence of additives is too poor to be utilized as printed circuit board manufacturing.[7)] Additives, such as alkali cyanides, 2,2′-bipyridyl, 1,10-phenanthroline, and 2-mercaptobenzothiazole, are practical for preventing the bath decomposition.[8)] On the other hand, additives such as 2,2′-bipyridyl,[9)] potassium cyanonickelate,[10)] and potassium hexacyanoferrate(II) ($K_4[Fe(CN)_6]$)[11)] are applicable to improve the foil quality. Simultaneous use of 2,2′-bipyridyl and $K_4[Fe(CN)_6]$ in the EDTA bath has been reported to be effective to improve the foil quality.[12)]

We have investigated the effects of 2,2′-bipyridyl in the TEA bath based on the adsorption model, and found that 2,2′-bipyridyl adsorbs onto the adsorbed TEA–Cu(II) complexes.[13)] In this study we examined the synergistic effects of 2,2′-bipyridyl and $K_4[Fe(CN)_6]$ on the foil quality and the plating rates in the TEA bath. We have found that the simultaneous use dramatically decreased the optimum concentration of respective additives to improve the quality. The adsorption process of 2,2′-bipyridyl and $K_4[Fe(CN)_6]$ was analyzed based on the adsorption kinetics.[5,6)]

Experimental

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, 2,2′-bipyridyl, and $K_4[Fe(CN)_6]$. The solution pH was adjusted to pH 12.8 by adding aqueous NaOH.

The plating rate dependence of the 2,2′-bipyridyl concentrations was measured at various Cu(II) and excess TEA concentrations. Since TEA used to form 1 : 1 complexes with Cu(II) ions,[14)] the TEA concentration exceeded the Cu(II) concentration was defined as the excess TEA concentration. The contribution of 1 : 2 complexes is negligible at high pH. The Cu(II) concentration was varied from 1.0×10^{-2} to 6.0×10^{-2} mol dm^{-3} and the excess TEA concentration from 1.2×10^{-1} to 1.0 mol dm^{-3}. After 5 and 10 min of plating at 60 °C, the plated substrates were weighed to determine the copper plating rate. Pretreatment of substrate and plating procedure are the same as described before.[5)] A scanning electron microscope (SEM) was used to observe the surface morphologies.

The mechanical properties of copper foils were evaluated using conventional tensile tester.[12)] Tensile test were performed according to IPC standard. All copper foils were annealed at 160 °C for 3 h after plating.[10,15)] The thickness of all foils was in the range of 30—35 μm.

Results

Surface Morphologies. Figure 1 shows the surface morphologies of deposit from the TEA bath in the presence of (a) 2.4×10^{-4} mol dm^{-3} $K_4[Fe(CN)_6]$ and 1.3×10^{-4} mol dm^{-3} 2,2′-bipyridyl, (b) 2.4×10^{-4} mol dm^{-3} $K_4[Fe(CN)_6]$, (c) 1.3×10^{-4} mol dm^{-3} 2,2′-bipyridyl respectively. The deposit quality from the TEA bath containing one of $K_4[Fe(CN)_6]$ or 2,2′-bipyridyl was not satisfactory. However, the simultaneous use of these two additives was effective to improve the quality. Figures 1c, 2a, 2b, 1a, and 2c show the $K_4[Fe(CN)_6]$ concentration dependence of the surface morphologies in the presence of 1.3×10^{-4} mol dm^{-3} 2,2′-bipyridyl. Although $K_4[Fe(CN)_6]$ higher than 4.7×10^{-4} mol dm^{-3} was required to obtain a good qual-

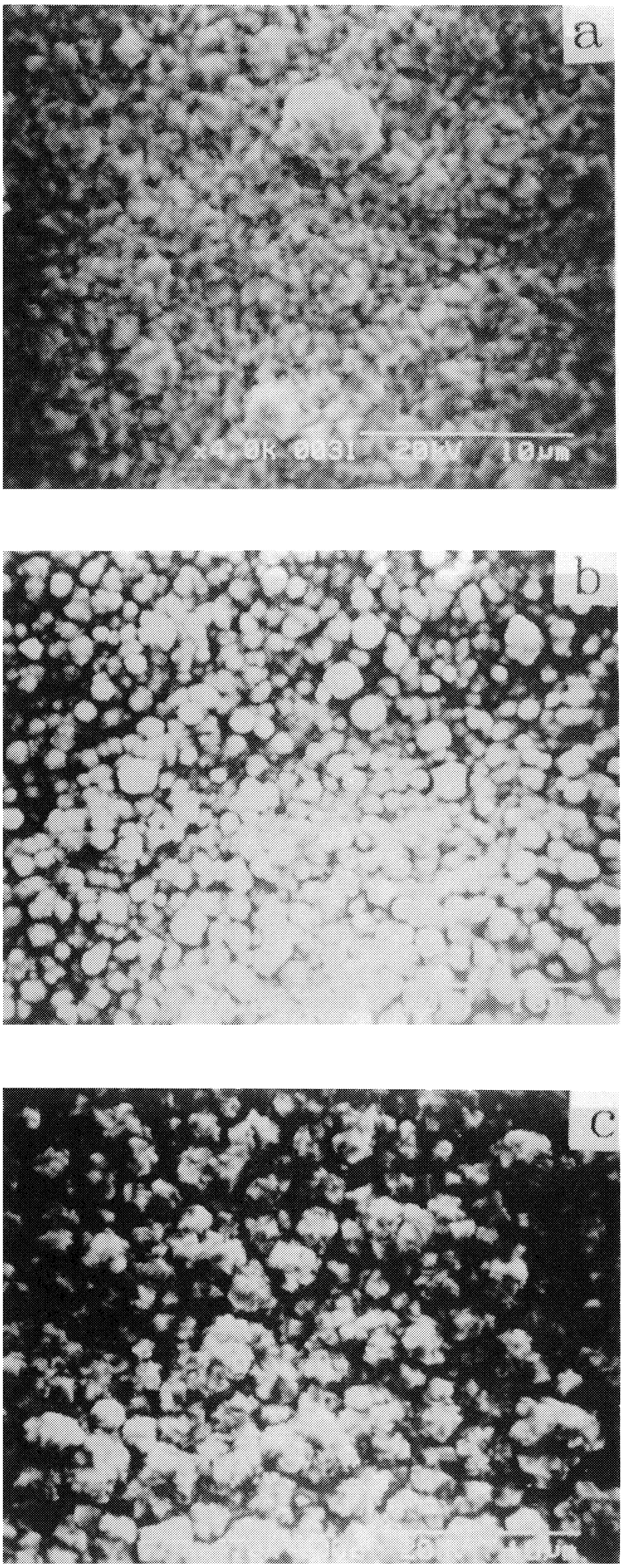

Fig. 1. Surface morphologies of TEA electroless copper deposited in the presence of the following additives concentrations: (a) 1.3×10^{-4} mol dm^{-3} 2,2′-bipyridyl and 2.4×10^{-4} mol dm^{-3} $K_4[Fe(CN)_6]$; (b) 2.4×10^{-4} mol dm^{-3} $K_4[Fe(CN)_6]$; (c) 1.3×10^{-4} mol dm^{-3} 2,2′-bipyridyl. The TEA baths contain 3.0×10^{-2} Cu(II) and 1.5×10^{-1} mol dm^{-3} TEA.

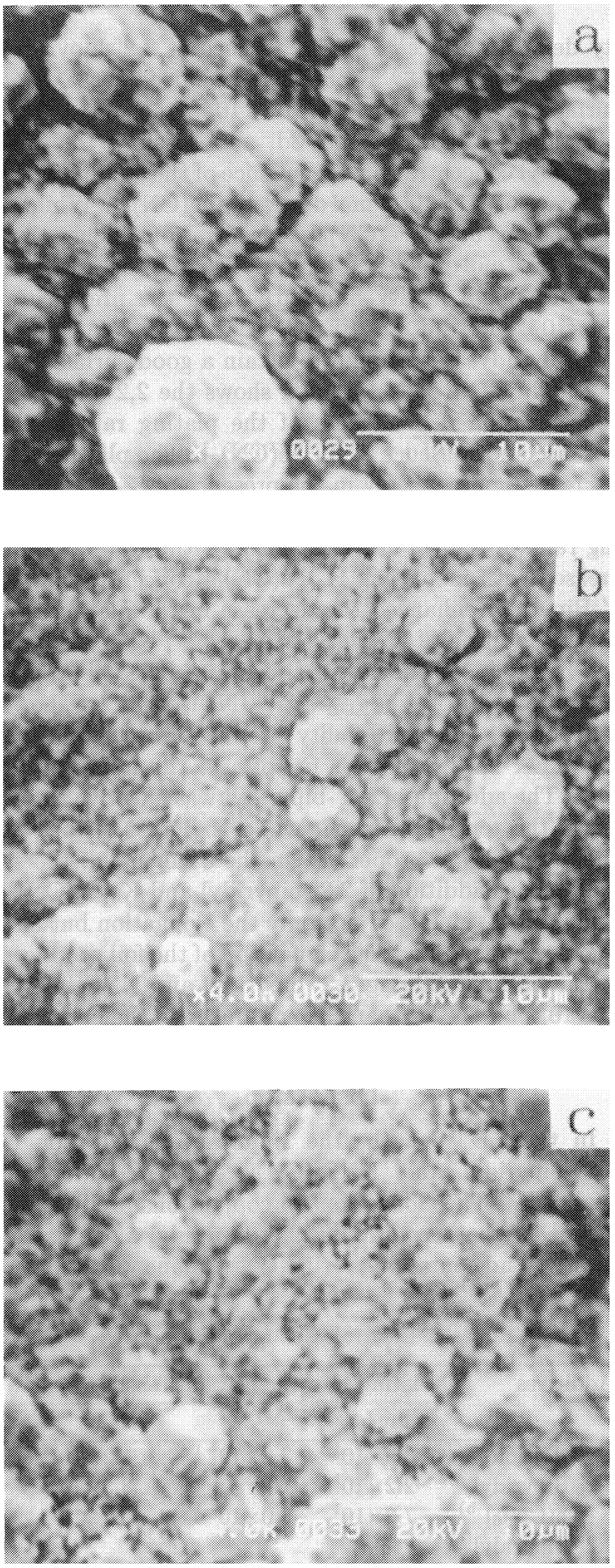

Fig. 2. Effects of $K_4[Fe(CN)_6]$ on the surface morphologies in the presence of 1.3×10^{-4} mol dm^{-3} 2,2′-bipyridyl. The $K_4[Fe(CN)_6]$ concentrations were as follows: (a) 5.0×10^{-5} mol dm^{-3}; (b) 1.4×10^{-4} mol dm^{-3}; (c) 7.1×10^{-4} mol dm^{-3}. The TEA baths contain 3.0×10^{-2} mol dm^{-3} Cu(II) and 1.5×10^{-1} mol dm^{-3} TEA.

ity deposit surface[13] in the absence of 2,2′-bipyridyl, 1.4×10^{-4} mol dm^{-3} $K_4[Fe(CN)_6]$ sufficed for a good surface in the presence of 1.3×10^{-4} mol dm^{-3} 2,2′-bipyridyl. Figures 3a, 2c, 3d, and 3c show the 2,2′-bipyridyl concentration dependence of the quality in the presence of 7.1×10^{-4} mol dm^{-3} $K_4[Fe(CN)_6]$. While in the absence of $K_4[Fe(CN)_6]$ concentrations higher than 6.4×10^{-4} mol dm^{-3} 2,2′-bipyridyl[13] were necessary to attain a high quality film surface, in the presence of 7.1×10^{-4} mol dm^{-3} $K_4[Fe(CN)_6]$ 1.3×10^{-4} mol dm^{-3} 2,2′-bipyridyl was enough to attain a good surface.

Plating Rate. Figure 4 shows the 2,2′-bipyridyl concentration dependences of the plating rate in the absence and presence of $K_4[Fe(CN)_6]$. The plating rate decreased more steeply in the presence of $K_4[Fe(CN)_6]$. The effects of $K_4[Fe(CN)_6]$ concentration on the plating rate are shown in Fig. 5. The plating rate also decreased with increasing $K_4[Fe(CN)_6]$ concentration. 2,2′-Bipyridyl enhanced the decrease in the plating rate by the addition of $K_4[Fe(CN)_6]$.

Physical Properties of the Foil. The foil properties obtained from the respective TEA baths are shown in Table 1. The foil quality produced in the additive free TEA bath was poor in spite of the high plating rate. The addition of 2,2′-bipyridyl was effective to improve the tensile strength, while $K_4[Fe(CN)_6]$ has no effect on the foil property. On the other hand, the simultaneous addition of 2,2′-bipyridyl and $K_4[Fe(CN)_6]$ dramatically increased not only the elongation but also the tensile strength. The elongation of the foil produced in the bath containing 2,2′-bipyridyl and $K_4[Fe(CN)_6]$ was 10 times larger than that produced in the bath containing 2,2′-bipyridyl alone as the additive.

Discussion

In the EDTA bath, the simultaneous addition of 2,2′-bipyridyl and $K_4[Fe(CN)_6]$ improved the foil quality.[9,12] The elongations of copper foils produced in the EDTA bath containing 2,2′-bipyridyl alone as the additive and containing $K_4[Fe(CN)_6]$ alone were 2.0 and

Table 1. Electroless Copper Properties

Additives	Plating rate	Elongation	Tensile strength
	µm h^{-1}	%	Pa
No addition	8.5×10^{1}	3.0×10^{-1}	1.2×10^{7}
2,2′-Bipyridyl [a]	2.2×10^{1}	1.2	3.5×10^{8}
$K_4[Fe(CN)_6]$ [b]	7.2×10^{1}	5.0×10^{-1}	6.2×10^{7}
2,2′-Bipyridyl [c] and $K_4[Fe(CN)_6]$	1.5×10^{1}	1.2×10^{1}	2.5×10^{8}

a) 6.4×10^{-4} mol dm^{-3} 2,2′-bipyridyl. b) 7.1×10^{-4} mol dm^{-3} $K_4[Fe(CN)_6]$. c) 6.4×10^{-4} mol dm^{-3} 2,2′-bipyridyl and 7.1×10^{-4} $K_4[Fe(CN)_6]$. Other components were as follows: 3.0×10^{-2} mol dm^{-3} $CuSO_4$, 1.5×10^{-1} mol dm^{-3} TEA, 8.0×10^{-2} mol dm^{-3} HCHO, and 1.8×10^{-1} mol dm^{-3} NaOH. Bath temperature was 60 °C.

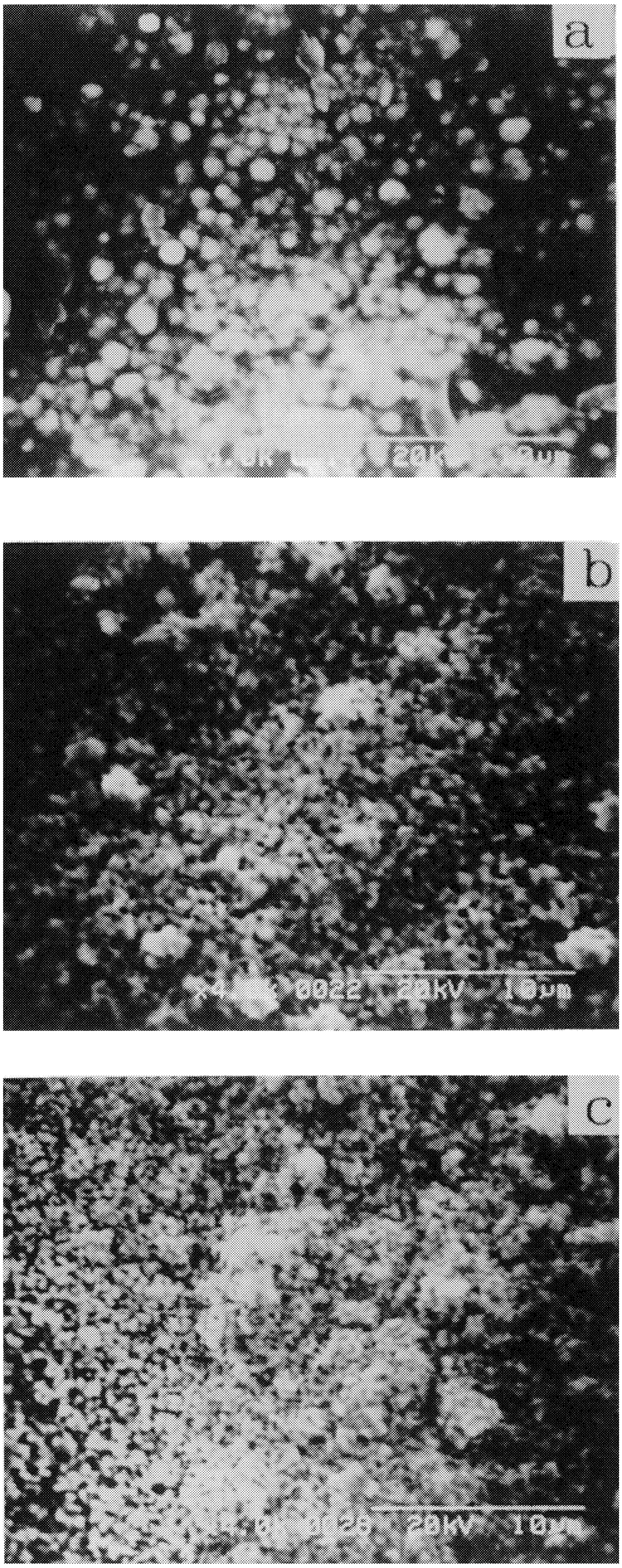

Fig. 3. Effects of 2,2′-bipyridyl on the surface morphologies in the presence of 7.1×10^{-4} mol dm^{-3} $K_4[Fe(CN)_6]$. The 2,2′-bipyridyl concentrations were as follows: (a) 0; (b) 3.6×10^{-4} mol dm^{-3}; (c) 1.3×10^{-3} mol dm^{-3}. The TEA baths contain 3.0×10^{-2} mol dm^{-3} Cu(II) and 1.5×10^{-1} mol dm^{-3} TEA.

Table 2. Summary of Data

	2,2′-Bipyridyl		$K_4[Fe(CN)_6]$	
	Alone	with $K_4[Fe(CN)_6]$ a)	Alone	with 2,2′-Bipyridyl b)
K_{a1} ($mol^{-1} dm^3$)	0.0	0.0	0.0	0.0
K_{a2} ($mol^{-1} dm^3$)	2.8×10^1	0.0	6.6×10^2	2.0×10^3
K_{a3} ($mol^{-1} dm^3$)	1.9×10^4	2.7×10^4	0.0	0.0

a) 7.1×10^{-4} mol dm^{-3} $K_4[Fe(CN)_6]$. b) 1.3×10^{-4} mol dm^{-3} 2,2′-bipyridyl.

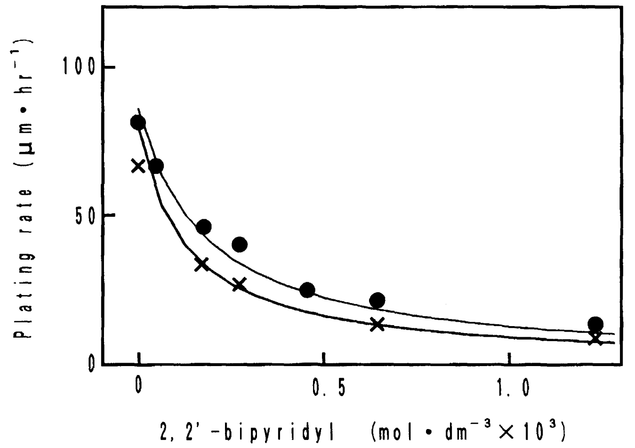

Fig. 4. 2,2′-Bipyridyl concentration dependences on the plating rate in the TEA bath containing 3.0×10^{-2} mol dm^{-3} Cu(II) and 1.5×10^{-1} mol dm^{-3} TEA: (●) in the absence of $K_4[Fe(CN)_6]$; (×) 7.1×10^{-4} mol dm^{-3} $K_4[Fe(CN)_6]$.

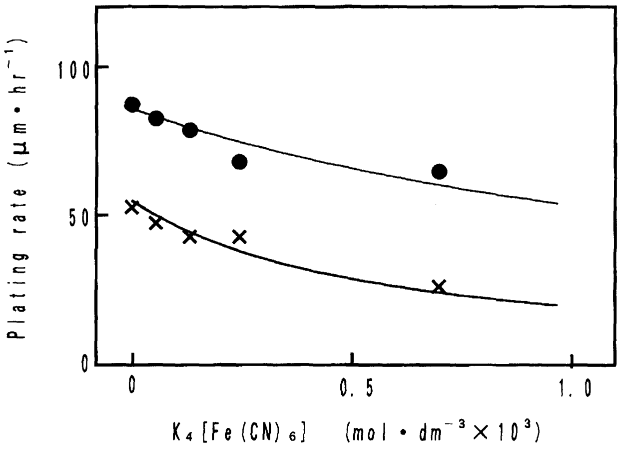

Fig. 5. $K_4[Fe(CN)_6]$ concentration dependences on the plating rate in the TEA bath containing 3.0×10^{-2} mol dm^{-3} Cu(II) and 1.5×10^{-1} mol dm^{-3} TEA: (●) in the absence of 2,2′-bipyridyl; (×) 1.3×10^{-4} mol dm^{-3} 2,2′-bipyridyl.

0.8% respectively, while the copper foil in the bath containing both 2,2′-bipyridyl and $K_4[Fe(CN)_6]$ had 5.5% elongation.[12] Osaka suggested that the synergistic effects is ascribable to the aggregates formation of 2,2′-bipyridyl and $K_4[Fe(CN)_6]$ on the reactive surface.[12] The synergistic effects in the TEA bath were larger than that observed in the EDTA bath as shown in Table 1. In order to reveal the mechanism of the synergistic effects, we analyzed the plating rate decreases by the addition of the additives based on the adsorption kinetics.

Adsorption- Kinetics. Figure 6 shows the adsorption model in the TEA bath.[5] In the TEA bath, excess TEA adsorbs onto the naked surface. The TEA–Cu(II) complexes adsorbs onto the adsorbed TEA and is reduced to Cu(0). TEA on the TEA–Cu(II) complexes inactivates against the reduction by formaldehyde. Three possible adsorption sites for additives are <1> on the naked surface, <2> on the adsorbed TEA, and <3> on the adsorbed TEA–Cu(II), as shown in Fig. 6. When additives adsorbs on the naked surface, the additives prevents the adsorption of TEA. The additives adsorbed on TEA interferes with the adsorption of TEA–Cu(II) complexes. Further additives on TEA–Cu(II) complexes inactivates Cu(II)→Cu(0) reduction.[13] The adsorbed TEA–Cu(II) complexes overlaid with neither excess TEA nor additives are reduced to Cu(0) with formaldehyde. The adsorption equilibrium constants of each process are expressed as K_{a1}, K_{a2}, and K_{a3} respectively.[13]

The plating rate is propertinal to the fractional surface converage of active TEA–Cu(II) complexes based on the adsorption model. Therefore the ratio of the rates in the presence of additives "r", and those in the absence of additives "$r_{Ca=0}$" is expressed as follows[13]:

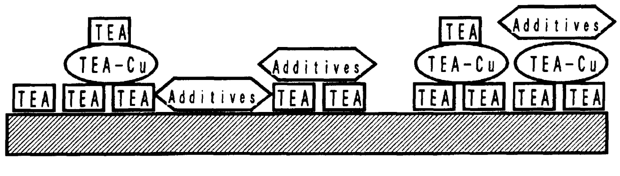

Fig. 6. Three possible adsorption sites for additives on the plating model.

$$\frac{\theta_3}{\theta_{3,\mathrm{Ca}=0}} = \frac{r}{r_{\mathrm{Ca}=0}} = \frac{(1+K_1C_{\mathrm{x1}})}{(1+K_1C_{\mathrm{x1}}+K_{\mathrm{a1}}C_{\mathrm{a}})} \times \frac{(1+K_3C_{\mathrm{c}})}{(1+K_3C_{\mathrm{c}}+K_{\mathrm{a2}}C_{\mathrm{a}})} \times \frac{(1+K_2C_{\mathrm{x1}})}{(1+K_2C_{\mathrm{x1}}+K_{\mathrm{a3}}C_{\mathrm{a}})} \quad (1)$$

where C_{x1}, C_{c}, and C_{a} are the concentrations of excess TEA, TEA–Cu(II) complexes, and additives, respectively; K_1 and K_2 are the adsorption equilibrium constants for excess TEA onto the naked surface and onto the adsorbed complexes, respectively; K_3 is the adsorption equilibrium constant of complexes onto the adsorbed TEA; θ_3 and $\theta_{3,\mathrm{Ca}=0}$ are the fractional surface coverages of active complexes in the presence and absence of the additives, respectively. The respective adsorption equilibrium constants for additives were determined by measuring the plating rate dependence on additives concentration.[13)]

By using K_1, K_2, and K_3 determined in the previous study,[5,6)] K_{a1}, K_{a2}, and K_{a3} were estimated from the optimum fits between the observed data and the calculated curves from Eq. 1. The calculated rates were represented by the solid curves of Figs. 4 and 5. As shown in Figs. 4 and 5, Eq. 1 reproduced well the additives concentration dependence of the plating rate. The values are summarized in Table 2 along with the values of 2,2′-bipyridyl alone.[13)]

Synergistic Effects of 2,2′-Bipyridyl and $K_4[Fe(CN)_6]$. As shown in Table 2, while 2,2′-bipyridyl adsorbs strongly onto the adsorbed TEA–Cu(II) complexes,[13)] $K_4[Fe(CN)_6]$ adsorbs only on the adsorbed TEA. The low adsorption activity of $K_4[Fe(CN)_6]$ on to the naked surface is ascribable to the high hydrophilicity. 2,2′-Bipyridyl effectively inactivates the adsorbed TEA–Cu(II) complexes by the direct interaction, while $K_4[Fe(CN)_6]$ competes with the complexes in the adsorption process to the adsorbed TEA and prevents the adsorption of the complexes. The difference in adsorption site between 2,2′-bipyridyl and $K_4[Fe(CN)_6]$ is considered to cause the difference in the deposit quality and the plating rate.

When 2,2′-bipyridyl and $K_4[Fe(CN)_6]$ were introduced simultaneously in the TEA bath, the respective adsorption equilibrium constants were increased as shown in Table 2. K_{a3} for 2,2′-bipyridyl and K_{a2} for $K_4[Fe(CN)_6]$ were about 1.5 and 3 times as large as the values in the bath containing one of the additives. The large K_{a3} and K_{a2} for respective additives enhanced the additive concentration effects on the plating rate. The increase in the adsorption equilibrium constants indicates that the adsorbed $K_4[Fe(CN)_6]$ interacts to some extent with the adsorbed 2,2′-bipyridyl. The interaction between adsorbed 2,2′-bipyridyl and $K_4[Fe(CN)_6]$ on the surface is considered to be effective to improve the metal foil property.

The authors wish to express their thanks to D. DiPietro for his kind corrections of English.

References

1) L. N. Schoenberg, *J. Electrochem. Soc.*, **119**, 1491 (1972); A. Hung, *J. Electrochem. Soc.*, **132**, 1047 (1985); M. Paunovic, *Plating (Paris)*, **1968**, 1161; F. J. Nuzzi, *Plat. Surf. Finish*, **70**, 51 (1983).

2) M. Paunovic, *J. Electrochem. Soc.*, **124**, 349 (1977); F. M. Donahue, D. J. Sajkowski, A. C. Bosio, and L. L. Schafer, *J. Electrochem. Soc.*, **129**, 717 (1982); W. Goldie, *Plating (East Orange, N. J.)*, **51**, 1069 (1964).

3) L. N. Schoenberg, *J. Electrochem. Soc.*, **118**, 1571 (1971).

4) K. Kondo, J. Ishikawa, O. Takenaka, T. Matsubara, and M. Irie, *J. Electrochem. Soc.*, **137**, 1859 (1990).

5) K. Kondo, J. Ishikawa, O. Takenaka, T. Matsubara, and M. Irie, *J. Electrochem. Soc.*, **138**, 3629 (1991).

6) K. Kondo, N. Ishida, J. Ishikawa, and M. Irie, *Bull. Chem. Soc. Jpn.*, **65**, 1313 (1992).

7) M. Matsuoka, S. Ito, and T. Hayashi, *J. Met. Finish. Soc. Jpn.*, **33**, 385 (1982).

8) M. Saito and H. Honma, *J. Met. Finish. Soc. Jpn.*, **29**, 88 (1978); E. B. Saubestre, *Plating (East Orange, N. J.)*, **59**, 563 (1973).

9) M. Saito and H. Honma, *J. Met. Finish. Soc. Jpn.*, **29**, 190 (1978); H. Honma and S. Mizushima, *J. Met. Finish. Soc. Jpn.*, **34**, 290 (1983).

10) Y. Okinaka and H. K. Straschil, *J. Electrochem. Soc.*, **133**, 2608 (1986); S. Nakahara, Y. Okinaka, and H. K. Straschil, *J. Electrochem. Soc.*, **136**, 1120 (1989).

11) R. Veleva, *Surf. Coat. Technol.*, **29**, 87 (1986).

12) H. Nagata, I. Koiwa, T. Osaka, and T. Yoshii, *J. Met. Finish. Soc. Jpn.*, **36**, 230 (1985).

13) K. Kondo, K. Kojima, N. Ishida, and M. Irie, *J. Electrochem. Soc.*, in press; K. Kondo, K. Kojima, N. Ishida, and M. Irie, *Chem. Lett.*, in press.

14) J. F. Fisher and J. L. Hall, *Anal. Chem.*, **39**, 1550 (1967).

15) S. Mizumoto, H. Nawafune, and M. Kawasaki, *J. Met. Finish. Soc. Jpn.*, **39**, 301 (1988).