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Kinetics of Electroless Copper Plating in the Presence of Excess Triethanolamine

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The electroless copper plating rate dependence on the various ligands, such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), *N,N,N',N'*-tetrakis(2-hydroxypropyl)-ethylenediamine (HPA), *N,N,N',N'*-tetrakis(2-hydroxyethyl)-ethylenediamine (HEA), triethanolamine (TEA), and triisopropanolamine (TIPA), were examined. TEA solution plating rate was the fastest of all ligands, the maximum rate being over 20 times faster than the current rate observed in the EDTA system. In order to reveal the rate dependence on the ligand, the adsorption equilibrium constants for Cu(II)-ligand complex onto the adsorbed ligand and the maximum deposition rates were determined based on the plating model previously proposed. The dependence was explained using the ligand adsorption equilibrium constant; (K_1) onto the reactive surface; (K_2) onto the adsorbed complexes and (K_3) the complex adsorption equilibrium constant.

Interest in electroless copper plating has recently been increasing because of its use in the manufacture of printed circuits and its potential application to many other processes. The present electroless copper plating process is useful for high quality copper plating, although a serious drawback is the low plating rate. In an attempt to increase the rate, the additives,[1–4] the ligands,[5] and coordination structures[6] have been investigated. However, sufficient acceleration has not been done yet.

The previous investigation[7] of various ligands, which was done to improve the electroless copper plating rate, resulted in the finding that excess triethanolamine (TEA) was extremely effective. The excess TEA increased the plating rate to over 20 times faster than the current rate observed in the ethylenediaminetetraacetic acid (EDTA) system. In order to consistently understand the ligand concentration dependence, we proposed a new plating model, and derived the adsorption-kinetics based on the model. Although the effects of excess ligand were interpreted by the adsorption of ligand on the reactive surface and that on the adsorbed Cu(II)-ligand complexes, the reason why TEA is the most effective among the ligands has not yet been clarified.

In the present study, the plating rate dependences on the ligands are investigated by adsorption-kinetics for Cu(II)-ligand complexes based on the plating model. The dependence is interpreted by the difference in the interaction between Cu(II)-ligand and adsorbed ligand on the reactive surface.

Plating Model. Figure 1 shows the model of the plating process.[8] All Cu(II) ions in solution are considered to exist in the form of 1 : 1 complexes.[9–15] The concentration of the 1 : 1 complex is constant in the presence of excess ligands. Interaction of excess ligands with 1 : 1 complexes in solution is negligible. We assumed that ligands adsorb on the reactive surface at first (Fig. 1A). This is because ligands are considered to be more active than 1 : 1 complexes. 1 : 1 complexes, then, adsorb on adsorbed ligands (Fig. 3B). The adsorbed 1 : 1 complexes are also overlaid with free excess ligands (Fig. 1C).

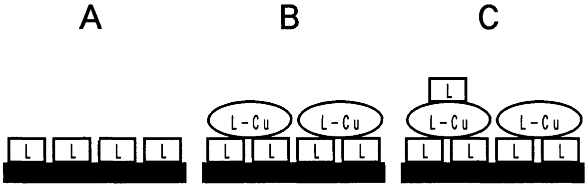

Fig. 1. Plating model on the reactive surface.

Adsorption-Kinetics. The adsorption-kinetics are derived by the above described plating model. It was assumed that all adsorption processes are equilibrated and follow Langmuir isotherm. Considering that the complex is inactivated by overlaid excess ligand, the fractional surface coverage of active complexes, θ_3, shown in Fig. 1C was expressed as

$$\theta_3 = \frac{K_1 C_{\mathrm{xl}}}{(1+K_1 C_{\mathrm{xl}})} \times \frac{K_3 C_{\mathrm{c}}}{(1+K_3 C_{\mathrm{c}})} \times \frac{1}{(1+K_2 C_{\mathrm{xl}})}, \qquad (1)^{8)}$$

where C_{xl} and C_{c} are the concentrations of excess ligands and complexes, respectively; K_1 and K_2 are the adsorption equilibrium constants for excess ligands onto the reactive surface and onto the adsorbed complexes, respectively; K_3 is the adsorption equilibrium constant of complexes onto the adsorbed ligands.

θ_3 shows a maximum with increasing C_{xl}. The maximum fractional surface coverage, $\theta_{3,\mathrm{max}}$, is expressed as follows

$$\theta_{3,\mathrm{max}} = \frac{K_3 C_{\mathrm{c}}}{1+K_3 C_{\mathrm{c}}} \times \frac{1}{(1+\sqrt{K_2/K_1})^2}\,. \qquad (2)$$

$\theta_{3,\mathrm{max}}$ increases with increasing C_{c}, or complex concentrations. When C_c is very large, the first term in Eq. 2 is equal to 1. Therefore the maximum value of $\theta_{3,\max}$ is expressed as $(\theta_{3,\max})_{\max}$.

$$(\theta_{3,\max})_{\max} = \frac{1}{(1+\sqrt{K_2/K_1})^2} \, . \qquad (3)$$

Under the assumption that the plating rate is proportional to the fractional surface coverage, the rate related to the concentration of complexes is expressed from Eqs. 2 and 3 as

$$\frac{\theta_{3,\max}}{(\theta_{3,\max})_{\max}} = \frac{r_{\max}}{R_{\max}} = \frac{K_3C_c}{1+K_3C_c} \, , \qquad (4)$$

where $r_{\max}$ is the plating rate at $\theta_{3,\max}$ when C_c is fixed at a certain value; $R_{\max}$ is the plating rate at $(\theta_{3,\max})_{\max}$, or the maximum value of plating rate. In other words, $R_{\max}$ is the theoretical value when the ideally adsorbed ligands are completely covered with the 1 : 1 complexes. Eq. 4 shows the plating rate dependences on the 1 : 1 complex concentrations, which is equal to the Cu(II) concentrations. The adsorption equilibrium constants for complex onto the adsorbed ligand (K_3) are determined by measuring the plating rate dependences on Cu(II) concentrations.

Experimental

The solutions were prepared with analytical grade reagents and deionized water. The electroless copper solution contained formaldehyde, NaOH, $CuSO_4$, complexing ligands for Cu(II), and additives. Other components are sumarized in Table 1. The ligands used in this experiment are as follows; TEA, triisopropanolamine (TIPA), nitrilotriaceticacid (NTA), *N*,*N*,*N*′,*N*′-tetrakis(2-hydroxyethyl)ethylenediamine (HEA), *N*,*N*,*N*′,*N*′-tetrakis(2-hydroxypropyl)ethylenediamine (HPA), and EDTA (Fig. 2).

The solution pH was adjusted to 12.8 by the addition of aqueous NaOH. Potassium ferrocyanide and 2,2′-bipyridyl were used as additives. The additives improved the properties of deposited copper film and the stability of solution.

The plating rate dependences on the excess ligands concentrations are measured at various Cu(II) concentrations. The Cu(II) concentrations were varied from 0.01 mol dm^{-3} to 0.08 mol dm^{-3}. The maximum plating rates were determined by fitting the Eq. 3 of previous report[8] to experimental data.

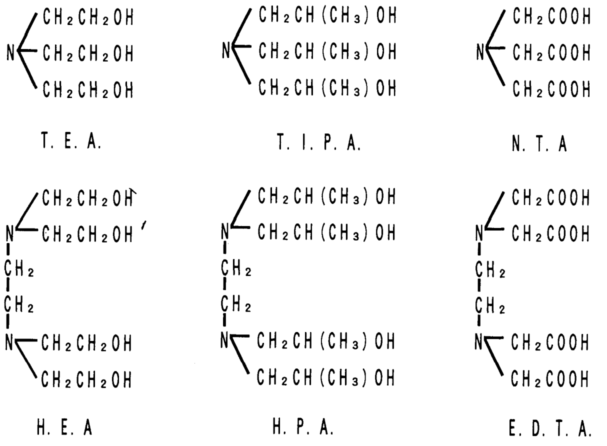

Fig. 2. Chemical structures of ligands.

Table 1. Electroless Copper Plating Solution

HCHO mol dm^{-3}	pH[a] at 25 °C	$K_4Fe(CN)_6$ ppm	2,2′-Bipyridyl ppm	Temp °C
0.22	12.8	20	10	60

a) pH=adjustor was NaOH.

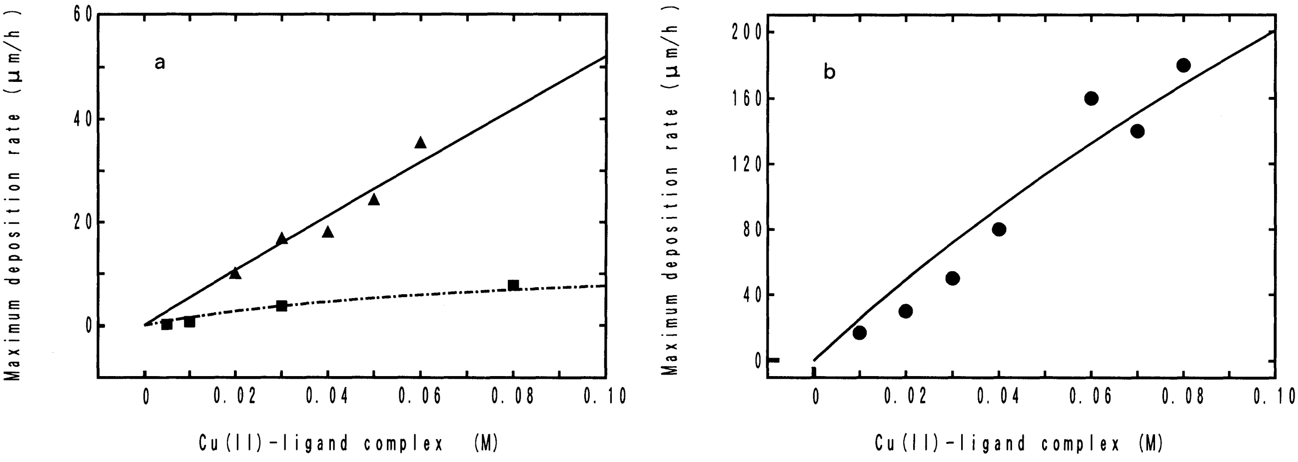

Fig. 3. Maximum plating rate dependence on the complex concentration using three different ligands: a (■) EDTA, (▲) HEA; b (●) TEA.

Table 2. Summary of Data

Ligand	K_1	K_2	K_3	R_{max}	r_{max}[a)]
	$mol^{-1}\times dm^{+3}$	$mol^{-1}\times dm^{+3}$	$mol^{-1}\times dm^{+3}$	$\mu m\ h^{-1}$	$\mu m\ h^{-1}$
EDTA	1.0×10^{-2}	1.0×10^{4}	1.2×10^{1}	1.4×10^{1}	7.7
NTA	1.0×10^{-2}	1.0×10^{4}	1.2×10^{1}	1.7×10^{1}	9.0
HEA	3.0×10^{3}	8.0	3.0×10^{1}	1.8×10^{3}	3.8×10^{1}
HPA	1.0×10^{3}	5.0	3.0×10^{-1}	1.5×10^{3}	3.2×10^{1}
TEA	1.0×10^{1}	2.0×10^{1}	3.0	8.7×10^{2}	1.8×10^{2}
TIPA	2.0×10^{1}	6.0×10^{1}	1.6	9.9×10^{2}	1.1×10^{2}

a) Cu(II)=0.08 mol dm^{-3}.

Pretreatment of substrate and plating procedure are the same as described before.7)

Results

Figure 3 a and b indicate the maximum plating rate dependences on 1 : 1 complex concentrations for EDTA, HEA, and TEA. Maximum plating rates increase with increasing complex concentrations. All curves derived from Eq. 4 reproduce the experimental results appropriately. The data obtained with other ligand solutions (TIPA, HPA, and NTA) were also reproduced by Eq. 4. K_3 and R_{max} were determined from the optimum fits between the observed data and the calculated curves. The values are summarized in Table 2 along with K_1 and K_2.

Discussion

The electroless copper plating rate is usually dependent on additives, ligands, and complex concentrations.3–5,16) Shippey and Donahue established an overall empirical rate law for electroless copper tartrate solutions,17,18) and Molenaar investigated the kinetics of EDTA solutions.19,20) In both tartrate and EDTA solutions, complex concentrations determine the plating rates, because the reduction process of cupric ion is rate determining.

In the previous study,7) we have shown that excess ligands, such as TEA, efficiently accelerate the plating rate. The excess ligand concentration dependences were explained by the adsorption equilibrium constants of ligand on the naked surface (K_1) and that on the adsorbed Cu(II)-ligand complexes (K_2).8) However, the plating rate dependence on the ligands was not explained yet. In order to reveal the dependence, it is necessary to measure the adsorption equilibrium constants for Cu(II)-ligand complexes (K_3). The plating rates for the various ligands are interpreted with K_1, K_2, and K_3.

As seen from Table 2, ligands with small K_1 such as EDTA and NTA have large K_2, while HEA and HPA with large K_1 have small K_2. The small K_1 for EDTA and NTA are ascribable to their hydrophilic properties at pH 12.8. Hydrophilic ligands scarcely adsorb on the naked surface, while they adsorb on polar adsorbed 1 : 1 complexes more efficiently than less polar HEA and HPA. TEA and TIPA have medial 1K_1 and K_2 values.

K_3 for EDTA and NTA is the largest among the examined ligands. The large K_3 value indicates a strong interaction between the adsorbed ligands and the 1 : 1 complexes. On the other hand, K_3 for HEA and HPA are much smaller than other ligands. The small K_3 value means that 1 : 1 complexes scarcely interact with the adsorbed ligands. Although Cu(II)–EDTA complexes easily adsorb on the adsorbed ligands, EDTA R_{max} was much smaller than TEA and HEA. This is explained as follows. EDTA scarcely adsorbs on the naked surface, and the adsorbed complexes are easily inactivated by the adsorption of free EDTA on the complexes, because K_1 is small and K_2 is large. The active complex concentrations remain at low values, even when complex concentration increases. On the other hand, the surface concentrations of active Cu(II)–TEA and –HEA complexes are large enough. Because both TEA and HEA easily adsorb on the surface and the ligands hardly inactivates the active complexes for large K_1 and small K_2.

Although Cu(II)–HEA K_3 is the smallest, R_{max} is the largest among the ligands examined. This is because the amount of Cu(II)–HEA adsorble sites is large, whereas K_1 is the largest and K_2 is the smallest. Therefore if the concentrations of Cu(II)–HEA were much larger, the plating rate would become very large; although this is not the case. In practice, the large r_{max} was not observed. The largest r_{max} was realized in TEA solution. The TEA large r_{max} is due to the large K_3.

It is interesting to compare the K_3 values between HEA and TEA. There is no difference in the interacting scheme between the adsorbed ligand and the Cu(II)-complexes in both HEA and TEA. The interactions between the complexes and the ligand are caused by the hydroxyl groups of ligand and the ionized groups of complexes.9,10,15,21) Therefore the large difference between HEA and TEA K_3 is owing to the geometrical structural difference of the molecules and the complexes. In other words, while a tetrahedral Cu(II)–TEA complex21,22) closely interacts with the adsorbed TEA molecule, an octahedral Cu(II)–HEA complex13,15,23) scarcely interacts with the adsorbed HEA molecule because of steric hindrance. The configuration of adsorbed ligands and complexes plays the most important role in the plating process.

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