Decomposition of citrate in electroless CoP baths

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The citrate concentration of electroless CoP plating solutions was found to decrease slowly with long-term use. The mechanism of citrate loss is most likely a thermal decarboxylation. In the electroless CoP solution, the decarboxylation reaction is catalyzed by the Co(II) ion and does not depend on any of the other solution components. The reaction occurs only in oxygen-containing solutions and its rate is limited by the rate of oxygen diffusion. The effect of other metal cations on citrate decomposition has been examined. Only those cations with a readily available 3+ oxidation state in aqueous solution seem to act as catalysts.

1. Introduction

Citric acid is a chemical of many industrial uses. Among these is its employment in the technology of electrodeposition. Its usefulness stems from its acid–base properties (it has three readily available protons with pK values of about 5.5, 4.4 and 3.1 for the three ionization reactions [1]) and from its ability to complex the cations of some technologically important metals [1]. Citrate is thus found as a complexant in a variety of electroless and electrolytic plating systems. Citrate is always regarded as stable under plating conditions, i.e. as not undergoing chemical changes. Routine analysis of CoP electroless plating solutions in daily use for periods in excess of 4 weeks has, however, shown an unexpected slow decrease in the citrate concentration. We have investigated some of the factors influencing citrate loss from electroless CoP solutions.

2. Experimental details

2.1. Electroless CoP solutions

The electroless CoP solution was an ammonia-free formulation at pH 8. It had the same components as one of the solutions described by Matsuda and Takano [2]: $CoSO_4$ as the source of Co(II), $Na_3C_6H_5O_7$ as the complexant, H_3BO_3 as the buffer and NaH_2PO_2 as the reducing agent. Experiments were done with two kinds of solution, at 'high' and 'low' citrate concentrations. The high-concentration solution allowed the study of citrate loss under actual conditions of CoP deposition. In the low-concentration solutions, the relative changes in the citrate concentration were

larger, and thus the low-concentration solutions allowed better sensitivity of the analytical techniques. The high-concentration solutions contained various combinations of the CoP components of the plating system at the same concentrations as in the working solution. The citrate concentration of the high-concentration solution was 0.1 M. The solutions for the low-concentration studies contained 5.3×10^{-3} mol l^{-1} $Na_3C_6H_5O_7$ (which is $1.0\,g\,l^{-1}$ $C_6H_5O_7^{3-}$) and one of the metal ions shown in Table 1.

2.2. Heating experiments

In order to study citrate loss during electroless plating, CoP was deposited on a NiP substrate of $\sim 75\,cm^2$ for a total of 60 h over several days. One litre of the solution was maintained at 80° C in a jacketed glass cell. The Co(II) and $H_2PO_2^-$ concentrations were adjusted based on the estimated rates of consumption of these chemicals during long-term operation of CoP baths. The pH was monitored and adjusted frequently.

Table 1. Cations investigated

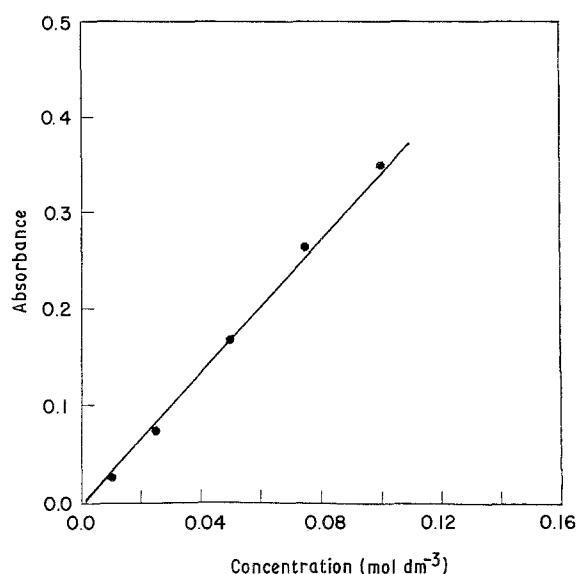| Ion		
Co(II)	4 mM	$1.00\,g\,l^{-1}$ as $CoSO_4 \cdot 7H_2O$
Co(II)	36 mM	$10.0\,g\,l^{-1}$ as $CoSO_4 \cdot 7H_2O$
Ni(II)	4 mM	$1.00\,g\,l^{-1}$ as $NiSO_4 \cdot 6H_2O$
Ni(II)	38 mM	$10.0\,g\,l^{-1}$ as $NiSO_4 \cdot 6H_2O$
Fe(II)	36 mM	$10.0\,g\,l^{-1}$ as $FeSO_4 \cdot 7H_2O$
Fe(III)	37 mM	$10.0\,g\,l^{-1}$ as $FeCl_3 \cdot 6H_2O$
Mn(II)	59 mM	$10.0\,g\,l^{-1}$ as $MnSO_4 \cdot H_2O$
Cr(VI)	100 mM	$10.0\,g\,l^{-1}$ as CrO_3

Fig. 1. The concentration dependence of the absorbance of citrate solutions at 190 nm. Solutions were diluted by a factor of 1000 before measurement. Quoted concentrations are before the 1 : 1000 dilution.
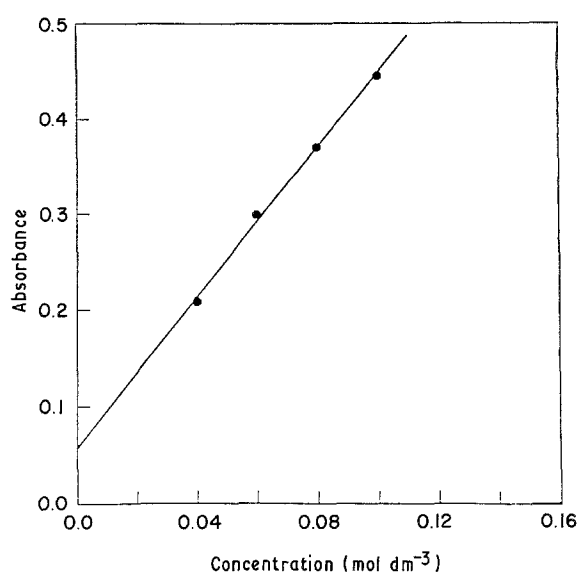
Fig. 2. The concentration dependence of absorbance of citrate solutions otherwise having the composition of the basic solution described in the Experimental section. Quoted concentrations are before the 1 : 1000 dilution.

The mixed potential was measured and did not change appreciably over the course of the experiment. The volume of the solution was maintained approximately constant through additions of d.i. H_2O.

For the experiments with no plating, 10-ml samples were heated in a dry incubator at 75–90° C for up to 250 h. The sample tubes were covered to prevent evaporation; the absence of a significant volume change was confirmed experimentally. Most of the experiments were performed in an air atmosphere. The effect of atmosphere was investigated by bubbling either N_2 or O_2 gas during the heating experiments. Measures were taken to prevent evaporation or loss of spray.

2.3. Spectrophotometric analyses

The high-citrate solutions were analyzed spectrophotometrically with an IBM Model 9420 UV/Vis spectrophotometer. All samples were diluted 1 : 1000 before analysis, but the concentrations are reported here as the values prior to dilution. The maximum absorption of citrate solutions occurs at 190 nm, the wavelength characteristic of absorption by carbonyl groups. At the 1 : 1000 dilution, none of the other solution components has a detectable absorption at 190 nm. There is also no evidence that the decomposition products of citrate influence the spectrum. The absorbance of citrate was found to obey Beer's Law over the concentration range examined, as shown in Fig. 1. Although the Co(II) does not absorb in the citrate region, it does influence the citrate absorption (a consequence of the complexation of Co(II) by citrate). Figure 2 shows the relationship between the 190-nm absorbance and the citrate concentration in a solution containing all of the components of the complete electroless CoP plating bath. The curve is linear, but the absorbances are somewhat higher than those in Fig. 1, and the curve does not pass through the

origin. The effect of varying cobalt concentration on the citrate absorbance is shown in Fig. 3. The solution absorbance at constant citrate concentration is increased by the addition of Co(II). None of the other components affects the citrate analysis. Because the
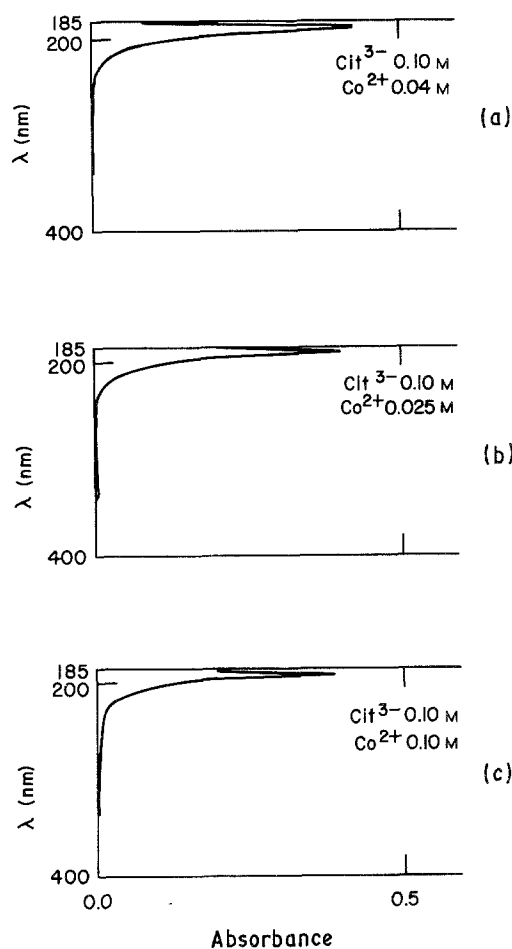

Fig. 3. The effect of Co(II) concentration on the absorbance of 0.10 M citrate solutions. (a) 0.04 M Co(II); (b) 0.025 M Co(II), (c) 0.01 M Co(II). Quoted concentrations are before the 1 : 1000 dilution.

Table 2. Citrate loss at 80° C. Per cent change in absorbance

Components	90 h	180 h	250 h
$C_6H_5O_7^{3-}$, Co(II)	16	15*	
$C_6H_5O_7^{3-}$, Co(II), H_3BO_3	20, 15	25, 27	31*
$C_6H_5O_7^{3-}$, Co(II), Pb(II)	~0	27	
$C_6H_5O_7^{3-}$, Co(II), Pb(II), H_3BO_3	10, 19	9, 27	
$C_6H_5O_7^{3-}$, Co(II), $H_2PO_2^-$	6	15*	
$C_6H_5O_7^{3-}$, Co(II), $H_2PO_2^-$, H_3BO_3	21, 23	16, 31	41*
$C_6H_5O_7^{3-}$, Co(II), $H_2PO_2^-$, Pb(II)	9	26*	
$C_6H_5O_7^{3-}$, Co(II), $H_2PO_2^-$, Pb(II), H_3BO_3	16	26	27*
$C_6H_5O_7^{3-}$, H_3BO_3	~1	~1	
$C_6H_5O_7^{3-}$, Pb(II)	~0	~1	
$C_6H_5O_7^{3-}$, $H_2PO_2^-$		~0	

* Sample precipitated. Supernatant was measured.

190-nm absorbance depends on Co(II) concentration, working calibration curves were constructed for solutions having approximately the same Co(II) concentration as the solution to be analyzed.

2.4. Ion chromatography

Citrate anion concentrations have been determined using mobile phase ion chromatography (MPIC) [3]. Citrate must be in the form of a free ion for accurate MPIC analysis. Citrate is freed from its complex with Co(II) by addition of the stronger complexant EDTA. A typical ion chromatogram of a CoP plating solution is shown in Fig. 4. The ion concentration is proportional to the area under the peak; for narrow peaks, the peak height is generally taken as a measure of concentration.

3. Results

3.1. Measurements in high-concentration solutions

Spectrophotometric analyses of electroless CoP solutions after up to 60 h of CoP deposition at 80° C showed no detectable loss of citrate, even though the total amount of metal deposited was relatively large. Much longer heating times in the absence of the electroless deposition reaction did succeed in producing

detectable citrate losses, however. In the complete CoP formulation, spectrophotometric analysis showed an ~ 50% reduction in the citrate concentration after 185 h of heating.

The effect of the solution components on citrate decomposition was examined by heating solutions of various combinations of these species at their working concentrations. The citrate concentrations of solutions heated at 80° C, determined by spectrophotometry, are given in Table 2. Citrate loss was observed only in solutions containing Co(II). The rate of citrate loss in solutions containing Co(II) plus combinations of the other solution components was not significantly different than the rate of loss in solutions containing Co(II) alone. Experiments were also done at 90° C (Table 3). Increasing the temperature did not significantly increase the rate of citrate loss. There is a scatter in the data of Tables 2 and 3, which is presumably the result of measuring a relatively small change in a large citrate concentration and of using the wavelength of 190 nm near the working limit of the instrument. Nonetheless, the above qualitative observations can be made based on these data.

In some solutions, precipitates formed upon heating. Precipitation was more likely to occur at long heating times or, at shorter heating times, in solutions not containing H_3BO_3. The precipitated samples were centrifuged before analysis of the supernatant solution. One of the precipitates was analyzed by spark emission and by SEM with energy-dispersive X-ray. In addition to Co, the precipitate contained detectable amounts of B from the H_3BO_3, P from the $H_2PO_2^-$ and Si (which was apparently leached from the glass test tubes). These analytical techniques give only
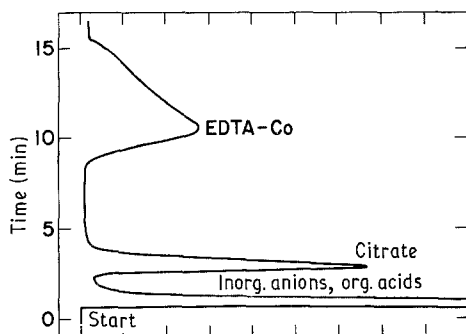

Fig. 4. Ion chromatogram of a CoP electroless solution. Column: AG 4a guard column and conductivity detector. Eluent: 0.01 M Na_2CO_3. $V = 2.5\,ml\,min^{-1}$.

Table 3. Citrate loss at 90° C. Per cent change in absorbance

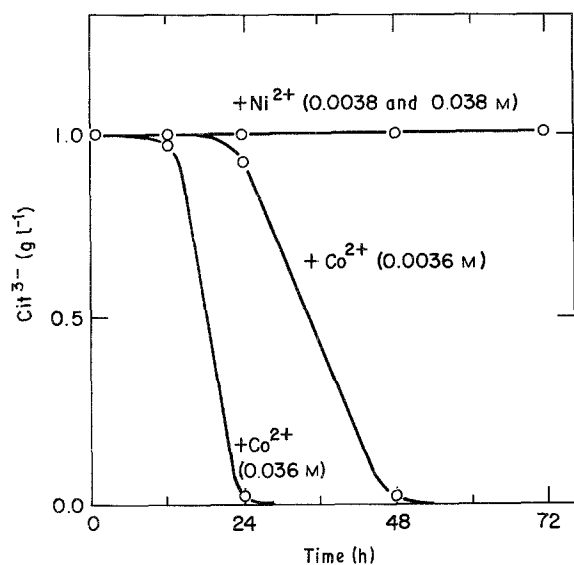| Components	90 h	180 h
$C_6H_5O_7^{3-}$, Co(II), H_3BO_3	12	9
$C_6H_5O_7^{3-}$, Co(II), Pb(II), H_3BO_3	13	24
$C_6H_5O_7^{3-}$, Co(II), $H_2PO_2^-$, H_3BO_3	15	14
$C_6H_5O_7^{3-}$, Co(II), $H_2PO_2^-$, Pb(II), H_3BO_3	11	17

Fig. 5. The time dependence of citrate concentration for solutions containing Co(II) and Ni(II). Temperature 75° C.
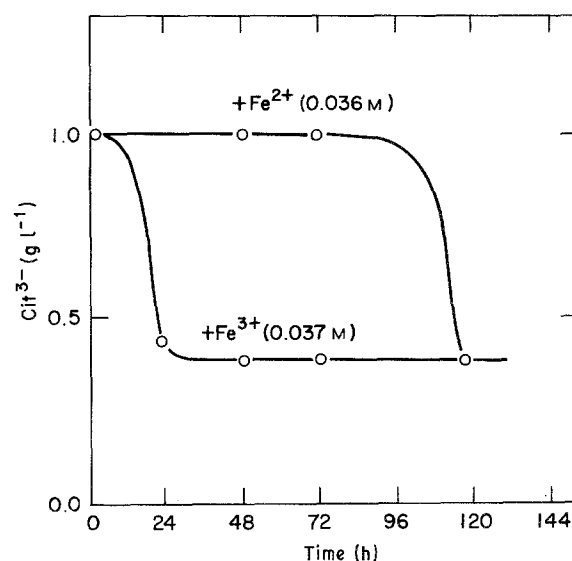

Fig. 6. The time dependence of citrate concentration for solutions containing Fe(II) and Fe(III). Temperature 75° C.

qualitative information, and thus the B, P and Si are assumed to be minor components in a precipitate that was not purified before analysis.

The effect of cations other than Co(II) was also examined. In these high-concentration citrate solutions, Co(II) was replaced by Cu(II); no citrate decomposition was observed in the presence of Cu(II). The atmosphere during heating was found to affect the rate of citrate decomposition. No citrate loss was observed in N_2-saturated solutions. In O_2-saturated solution, large amounts of dark-colored precipitates formed.

The heating experiments in high-concentration solutions were complemented by cyclic voltammetry at room temperature and at 80° C. Both Co and Ni electrodes were used. Comparison of the curves in citrate-free solutions with those in solutions containing citrate showed no evidence of an electrochemical reaction of citrate under the conditions of the experiment.

3.2. Measurements in low-concentration solutions

Typical measurements of citrate decomposition in low-concentration solutions, as determined from MPIC analysis, are shown in Figs 5 and 6. The citrate concentration is given as a function of the time of incubation at 75° C. The rate of change of citrate concentration depends strongly on the cation present. There is no citrate loss from Ni(II) solutions (Fig. 5). Citrate loss is significant in Co(II) solution (Fig. 5), the rate of loss increasing with increasing Co(II) concentration. Iron cations also cause citrate decomposition, the rate of loss being greater in Fe(III) solutions than in Fe(II) solutions; it is possible that only the Fe(III) oxidation state is active and that the delay before the onset of citrate loss in Fe(II) solution is the time required for atmospheric oxidation of Fe(II) to Fe(III). The effect of Mn(II) (not shown) is similar to that of Fe(III) or of Co(II) at $10 \, \mathrm{g} \, l^{-1}$. Citrate decomposition is not observed in Cr(VI) solution (also not shown).

The greatest citrate losses in the low-concentration solutions were, like those in the high-concentration solutions, often accompanied by the formation of a precipitate. The olive-green precipitate did not contain citrate. The precipitate from the Co(II)-containing solution was found to contain 50.7% cobalt, very nearly the 49.6% cobalt expected in cobalt carbonate.

4. Discussion

Although both chemical and electrochemical reactions of citrate ions are possible, only a homogeneous chemical decomposition appears to account for citrate loss from electroless CoP plating solutions. At the pH of these solutions, essentially all of the citric acid/citrate is in the form $C_6H_5O_7^{3-}$. The electrooxidation of carboxylic acids (the Kolbe reaction) is well known [4], but it is assumed to be unlikely at the relatively negative potentials of electroless deposition. Electroreduction of carboxylic acids does not occur unless the carboxyl group is strongly activated by an electron-withdrawing group [5]. Electroreduction is also assumed to be unlikely because it is not observed in plating solutions containing citrate. The assumption that the mechanism of citrate loss is not electrochemical is supported by the observation that the reaction proceeds in the absence of ongoing electroless CoP deposition and by the cyclic voltammetry experiments, which showed no indication of an electrochemical reaction of citrate.

The most probable chemical reaction of citrate is thermal decarboxylation. Many carboxylic acids are known to undergo thermal decarboxylation [4]. The mechanism is probably different for different acids; in some cases, it may be facilitated by the possibility of ring formation [4]. Metal-catalyzed decarboxylation is also known [6]; the metal ion can act as an electron withdrawer to facilitate the reaction. The observations support a metal-catalyzed decarboxylation as the mechanism of citrate decomposition: the rate of citrate loss

is strongly dependent on the metal cation; and the formation of the precipitate, which is apparently cobalt carbonate, is the result of CO_2 evolution during the decarboxylation reaction.

The metal-catalyzed citrate decomposition does not occur in the presence of Cu(II), Ni(II) or Cr(VI) but does proceed in the presence of Co(II), Fe(II), Fe(III) and Mn(II). The cations that promote the citrate decomposition have in common the ready availability of a 3+ oxidation state. Although neither Co(III) nor Mn(III) is stable as a simple ion in aqueous solution, the 3+ oxidation states of these metals are known to be stabilized by complexation. Dissolved oxygen can provide the oxidizing potential to form the 3+ ion from the original 2+ state in solution. The strong electron-withdrawing power of the 3+ oxidation state may facilitate the thermal decarboxylation of citrate.

Oxygen is a reactant in the citrate decarboxylation, and indeed citrate loss does not occur in N_2-saturated solutions. In unstirred solutions in contact with air, the rate of reaction is limited by the rate of diffusion of O_2. This diffusion limitation of the reaction accounts for the observation that the rates of citrate loss are nearly the same at 80 and 90° C. When O_2 is actively bubbled through the solution, the copious formation of a carbonate precipitate indicates a much higher rate of citrate decomposition.

5. Conclusions

The loss of citrate in electroless CoP solutions most likely occurs by way of a slow homogeneous chemical reaction, presumably a thermal decarboxylation. The thermal decarboxylation reaction is catalyzed by the metal cation in solution. An available 3+ oxidation state appears to be required. This high positive oxidation state is probably necessary to provide sufficient electron-withdrawing power to activate the carboxyl group. In Co(II)-containing solutions, O_2 was shown to be necessary to the reaction. It seems that the O_2 provides the potential to oxidize Co(II) to Co(III) and that, by analogy, O_2 is also instrumental in forming the 3+ oxidation state of the other cations that catalyze the citrate-decomposition reaction.

Acknowledgements

References

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