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THE INFLUENCE OF FLUORIDE ION ON THE CURRENT EFFICIENCY OF PULSE PLATING OF COPPER

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SUMMARY

This investigation is concerned with the effect of fluoride ion additives on the current efficiency of copper deposition under conditions of pulsed current. The parameters include the pulsating current density and the off - time duration. Fluoride - containing electrolytes were found to have higher current efficiency than the acidic copper sulfate electrolyte. A model based on a successive charge transfer process was proposed to explain the experimental observations. Fluoride ions can complex with cuprous ions to prevent its disproportionation, which results in a higher current efficiency.

INTRODUCTION

Pulse plating, because it has more process parameters for control and higher instantaneous current density than direct

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current, has received much attention in recent years[1-7]. Two advantages were most frequently cited by investigators in this field [8-17]. Firstly, a higher average current density for deposition can be applied to the plating system because of higher average concentration of metal ion in the diffusion layer. Secondly, a fine-grain deposit can be obtained by proper adjustment of the operation parameters, involving on-time, off-time and current density.

Other than change in physical properties due to pulse plating, its effect on current efficiency is another important research area. Wan et al. [18] studied the cathodic current efficiency of the copper plating in a copper sulfate solution and found that the efficiency could drop from nearly 100 % to values ranging from 80 % to 94 % for current pulses in the millisecond range. A mathematical model [19] was formulated to explain the behavior of this acidic copper sulfate system under pulsed current conditions. In this model, the deposition of Cu^{2+} is assumed to occur via a two-step mechanism according to the following equations:

$$Cu^{2+} + e \longrightarrow Cu^{+} \qquad (1)$$

$$Cu^{+} + e \longrightarrow Cu \qquad (2)$$

$$2Cu^{+} \longrightarrow Cu^{2+} + Cu \qquad (3)$$

In pulsed plating, some of the Cu^{+} ions in Eq.(1) go through Eq.(3) and form elemental copper suspended in the electrolyte during the off period, which results in lowering of the current efficiency.

Most of the reports regarding pulse plating have been restricted to systems without additives presumably to simplify the analysis. However, in real plating practice, it is very common to add various ingredients to change the properties of the deposit or the plating process.

It has been reported [20] that electroplating solutions containing fluoride ion could deposit metals at higher speed, i.e. at current densities considerably above the current density of a system containing only the same amount of metal ions.

Hence, a combination of pulsed current and fluoride ion additive could potentially produce further changes in a copper plating system. This has so far not been fully studied. In the present study, we investigate the effect of fluoride ion on the current efficiency of copper plating systems under pulsed current conditions.

EXPERIMENTAL

A rectangular cell($9 \times 5 \times 8$ cm^3) made of lucite was used as the plating cell. Copper panels with fcc crystallites were used as cathodes. The anodes were pure copper plates. All the electrolytes were prepared with reagent grade chemicals and deionized water. The plating bath compositions are recorded in Table 1.

Plating was carried out at room temperature (22-28°C) in a stirred solution with a magnetic stirrer controlled at about 300 rpm. The square-wave current pulse was generated by a direct current power supply which was connected to an interface controlled by a microcomputer (IBM-PC & AD 500A Programmable Multifunction Unit). An oscilloscope (Hitachi Digital Storage Oscilloscope VC-6020) was used to measure the current or potential response. A block diagram of the apparatus is shown in Fig. 1.

TABLE 1

Composition of plating bath, concentration (M)

constituent	bath A	bath B	bath C	bath D	bath E
CuF_2	0.477	......	......	......	......
$CuSO_4$	......	0.477	0.477	0.801	......
$Cu(ClO_4)_2$	......	......	......	......	0.801
HF	0.909	......	......	......	......
H_2SO_4	......	0.909	0.909	0.510	......
$HClO_4$	......	......	......	......	0.510
NaF	......	......	1.0	......	......

The current efficiency is the ratio of electricity consumed in the copper deposition to the total number of coulombs applied. The total applied coulombs were calculated by measuring the on-time, off-time and the pulsating current in a period and the total number of pulses. The effective coulomb for copper deposition was measured by gravimetric methods.

Cathodic polarizations were measured with a saturated calomel electrode as reference.

The fluoride content in the copper deposit was examined by ESCA (Perkin-Elmer PHI 548).

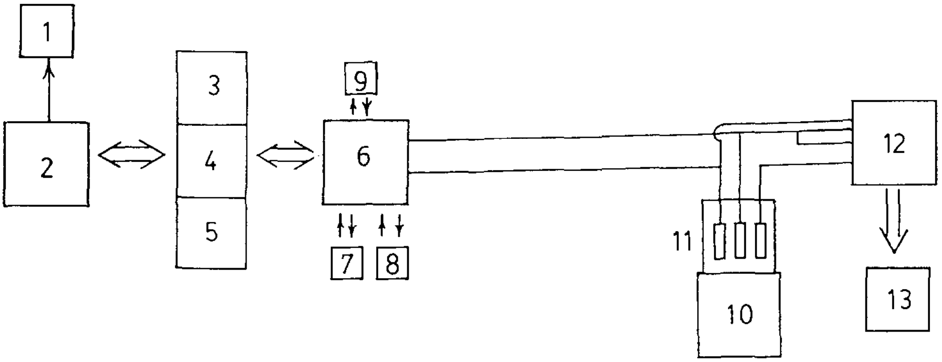

Fig. 1. Block diagram of the pulsed current system. (1) printer (2) pc (3) digital output (4) timer (5) counter (6) interface (7) power supply (8) adjustor (9) function generator (10) stirrer (11) cell (12) oscilloscope (13) recorder.

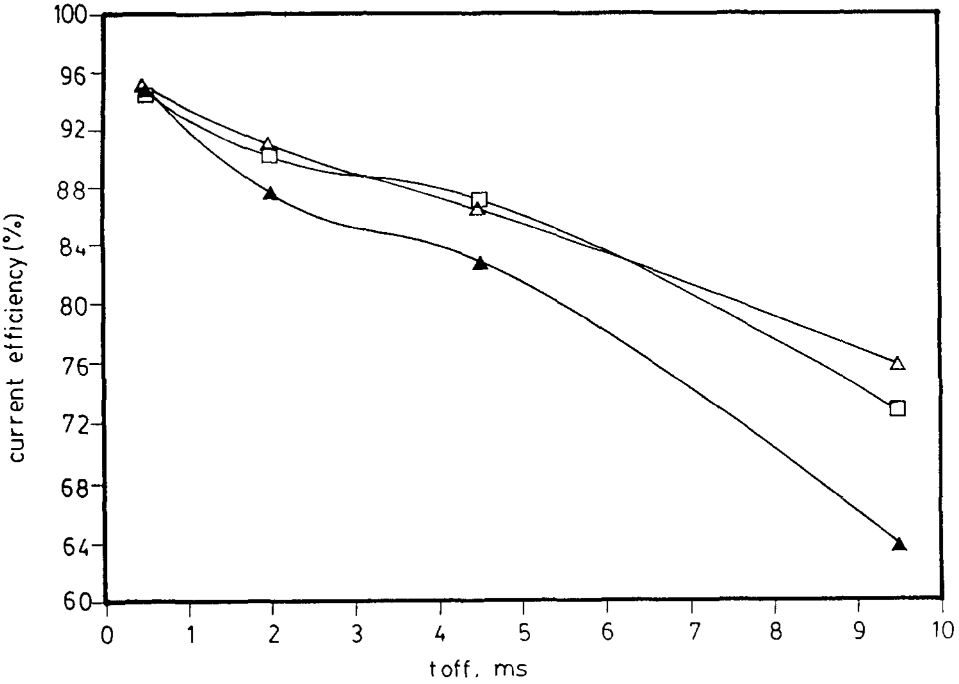

Fig. 2. Cathodic current efficiency versus t_{off} with a constant t_{on} (0.5 ms) and a constant pulse current density (5.12 ma/cm^2). △: bath A, ▲: bath B, □: bath C.

The diffusion coefficient of Cu^{2+} in the electrolyte is an important coefficient in our proposed model. It was measured by a potentiostatic method [21] with a rotating disc electrode (Pine RDE 4) which has a 0.164cm^2 working area. Platinum wire and SCE were used as counter electrode and reference electrode respectively. The compositions of all the electrolytes are in Table 2. The copper ion concentration of the electrolytes was determined by atomic absorption spectrophotometry (Varian SpectrAA 30).

TABLE 2

Composition of electrolytes, concentration (M)

constituent	bath F	bath G	bath H	bath I
CuF_2	0.05	......	......	......
$CuSO_4$	......	0.05	0.05	0.05
HF	0.095	......	......	......
H_2SO_4	......	0.095	0.095	0.095
NaF	......	......	0.1	0.2

The mobility of the Cu^{2+} ion in the electrolyte was measured by paper electrophoresis [20][22] (Camag, HVE system). We used a 0.01 M acetic acid solution (pH = 4.0) as buffer and applied a voltage gradient of 11.1 v/cm with a transit time of 2 hr. The developers used to define the spot position in the electrophorograms were an aqueous saturated solution of sodium diethyldithiocarbamate for copper.

RESULTS AND DISCUSSION

(1) Variation of current efficiency in response to the length of t_{off} and current density

The effect of t_{off} on the current efficiency of different electrolytes is shown in Figure 2. The current efficiency generally decreases as t_{off} lengthens, which is consistent with the previous finding [18]. Furthermore, it is clear that fluoride - containing electrolytes have higher efficiency than the pure acid copper sulfate solution. For example, at t_{off} equal to 9.5 ms, baths A, B and C have current efficiencies of 75.7 % , 63.8 % and 72.6 % respectively. When the t_{off} is only 0.5 ms, all systems approach a direct current process and according to Fig.2, the current efficiency of a fluoride -containing electrolyte (bath A or bath C) is about equal to that of a pure acid copper electrolyte (bath B) at t_{off} =0.5 ms. This means that the difference of current efficiency when t_{off} is larger than 4.5 ms is the result of a combination of the fluoride additive and pulse current rather than the effect of fluoride ions alone.

When we increased the current density to 81.96 ma/cm^2, the current efficiencies of baths A , B and C are shown in Fig.3. Although the current efficiency shows little difference with t_{off} less than 4.5 ms, the current efficiency of fluoride-containing electrolyte is again definitely higher than the pure acid copper electrolyte when t_{off} is longer than 4.5 ms. For example, with a 9.5 ms t_{off}, baths A, B and C have current efficiencies of 94.1 % , 88.3 % and 92.2 % respectively.

The current efficiencies of these three baths as a function of the pulse current density are shown in Figures 4 and 5. From

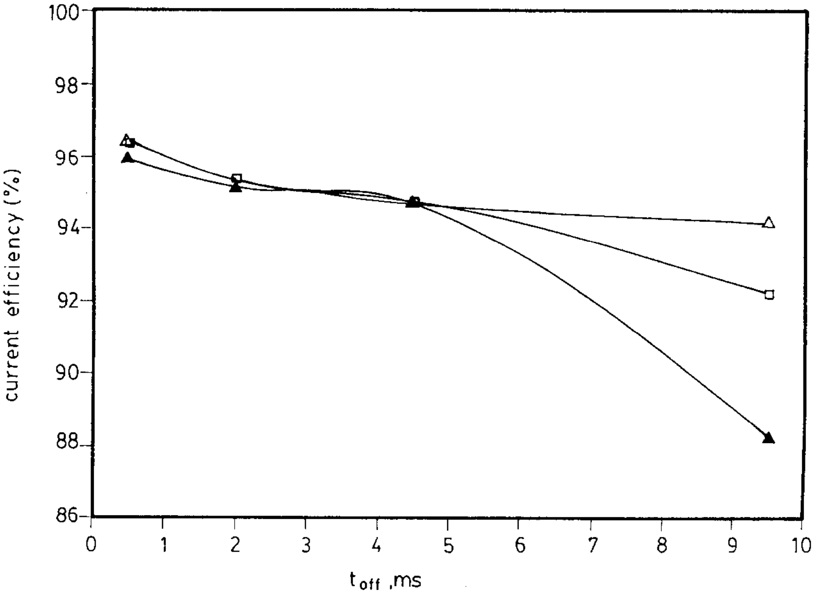

Fig. 3. Cathodic current efficiency versus t_{off} with a constant t_{on} (0.5 ms) and a constant pulse current density (81.96 ma/cm^2). △: bath A, ▲: bath B, □: bath C.

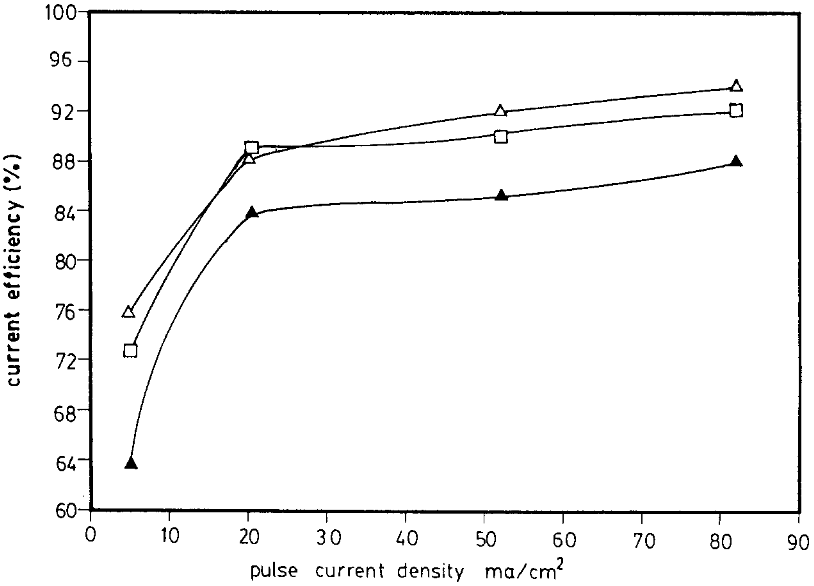

Fig. 4. Cathodic current efficiency versus pulse current density with a constant t_{on} (0.5 ms) and a constant t_{off}(9.5 ms). △: bath A, ▲: bath B, □: bath C.

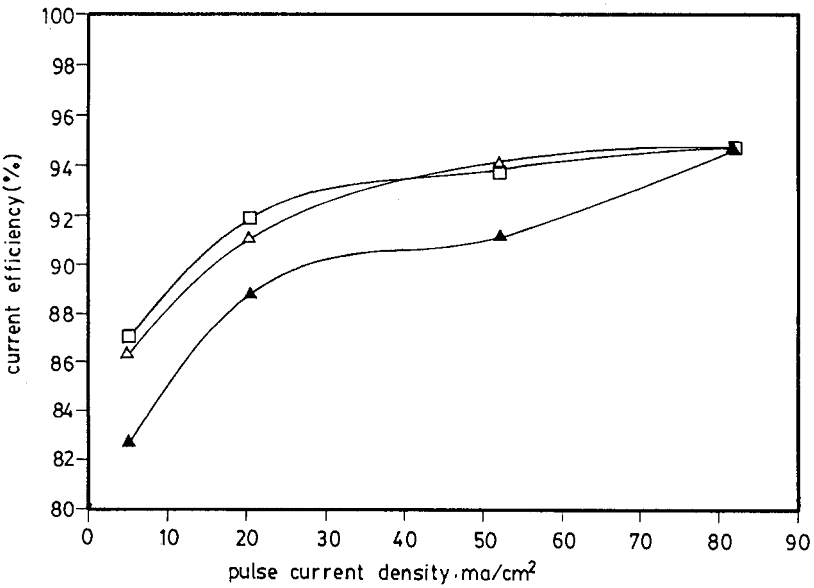

Fig. 5. Cathodic current efficiency versus pulse current density with a constant t_{on} (0.5 ms) and a constant t_{off}(4.5 ms). △: bath A, ▲: bath B, □: bath C.

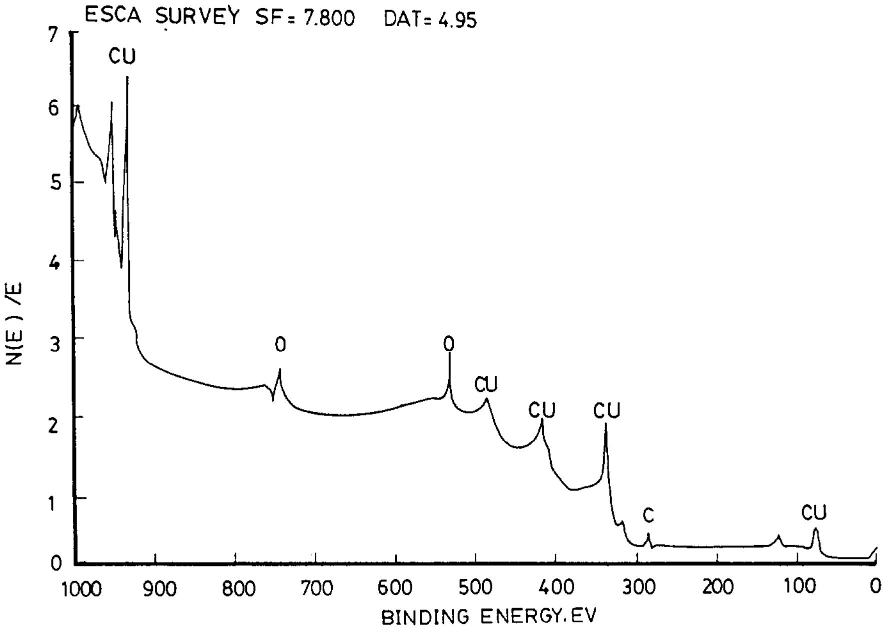

Fig. 6. ESCA measurement of deposits of fluoride-containing baths.

the figures, the current efficiency of pulsed current with a 0.5 ms t_{on} and a 9.5 ms or 4.5 ms t_{off} increases with pulsed current density. The fluoride-containing electrolytes consistently have higher current efficiency than the pure acid copper sulfate solution. Why the fluoride ions can increase the current efficiency is explained in the next section.

(2) Reaction mechanism

The electrodeposition of copper proceeds through four distinct steps [23-27]:

$Cu^{2+}_{(aq)} \longrightarrow Cu^{2+}_{(surf)}$ (4) mass transport step
$Cu^{2+}_{(surf)} \longrightarrow Cu^{+}_{(ad)}$ (5) first charge transfer step
$Cu^{+}_{(ad)} \longrightarrow Cu_{(ad)}$ (6) second charge transfer step
$Cu_{(ad)} \longrightarrow Cu_{(cry)}$ (7) surface diffusion step

where $Cu^{2+}_{(surf)}$ means cupric ions near the Helmholtz boundary layer in adjacent to the electrode surface, $Cu^{+}_{(ad)}$ means cuprous ions adsorbed on the crystal plane, $Cu_{(ad)}$ means copper atom adsorbed on the crystal plane and $Cu_{(cry)}$ means deposit crystal of copper.

Mattsson and Bockris [23] studied copper deposition in a pure acid copper electrolyte and concluded that surface diffusion is the rate determining step at low current density and that the first charge transfer step is the rate determining step at high current density. However, Ivanova [20] mentioned that the mobility of copper(II) ions in the electrolyte also has an important influence on the mechanism. Therefore, we attempted to investigate the relative importance of mass transport, charge transfer and surface diffusion in order to explain the effect of fluoride additive on the current efficiency in pulsed plating.

At first, we suspected that fluoride was incorporated in the deposit matrix and caused a change in surface activity, which in turn resulted in an increase in current efficiency. However we could not detect fluorine from ESCA data (Fig.6, binding energy of fluorine is 186 EV from ESCA manual's data (Perkin-Elmer)) and therefore ruled out this possibility.

The mass transport in electrolytes are controlled by convection, diffusion and migration. Within the diffusion layer, we only consider the diffusion and migration processes. We then attempted to evaluate the diffusion coefficient and mobility of copper (II) in various baths and tried to find a correlation between these transport parameters and the current efficiency.

The diffusion coefficient can be determined with an RDE system and ionic mobility can be determined from paper electrophoresis measurements. From Fig.7, the limiting currents(i_l) of four baths are proportional to the square root of rotation speed ($w^{1/2}$) and obey the following equation,

$$i_l = a + b\,w^{1/2} \qquad (8)$$

The small values of 'a' have no physical significance and are probably due to the anomalous experimental effects discussed by Adams [28] and Riddiford [29]. The diffusion coefficient can then be calculated from the value of 'b' according to Levich's equation [21]. The results in Table 3 show that the diffusion coefficient of Cu^{2+} in bath F is more than twice that in bath G. But in baths H and I which both contain fluoride ions, the diffusion coefficients are actually smaller than that in bath G which contains no fluoride ions.

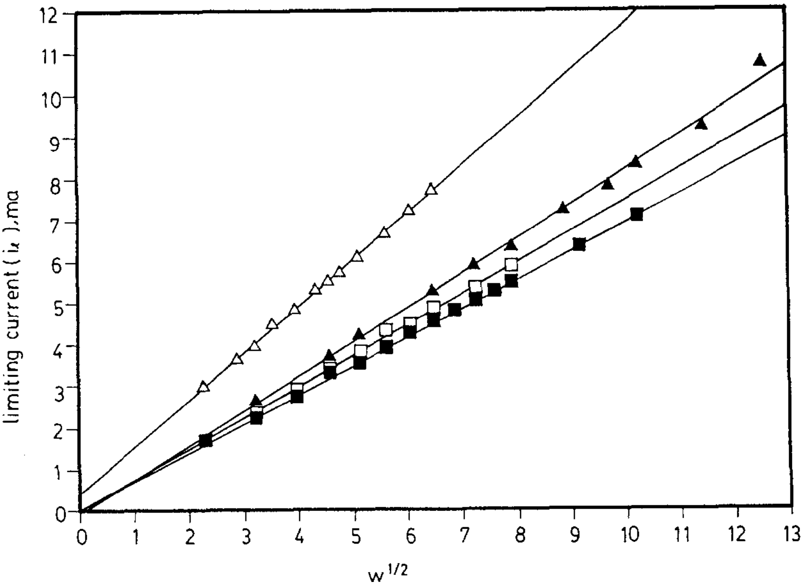

Fig. 7. Regression lines describing i_l versus $w^{1/2}$ behavior of different baths electrolyzed at a RDE. △: bath F, ▲: bath G, □: bath H, ■: bath I.

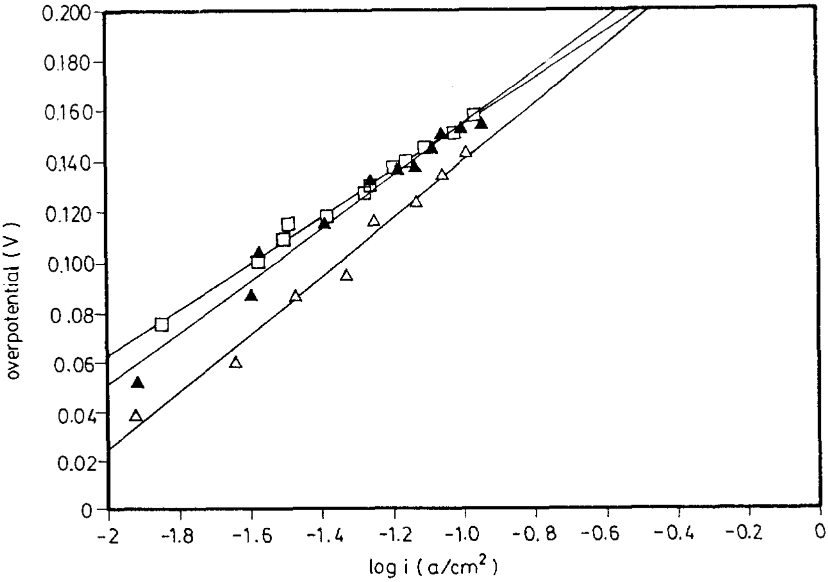

Fig. 8. Tafel line of copper deposition of different baths. △: bath A, ▲: bath B, □: bath C.

TABLE 3

Cu^{2+} Diffusion coefficient for different baths

$D_{Cu^{2+}}$,in	bath F	bath G	bath H	bath I
10^6.cm^2/sec	13.31±0.18	6.22±0.02	5.19±0.07	5.03±0.05

Figures 2 and 3 show that all electrolytes containing fluoride ions definitely have higher current efficiency than bath B. Therefore, the diffusion process cannot be the controlling factor in affecting the current efficiency, as no correlation can be found between the magnitude of diffusion coefficient and current efficiency.

The mobilities of cupric ions in baths A, B and C are reported in Table 4.

TABLE 4

Mobility of Cu^{2+} for different baths

$u_{Cu^{2+}}$,in	bath A	bath B	bath C
10^5.cm^2/v.sec	2.54	8.61	7.16

We can see that the Cu^{2+} mobility in bath A is much smaller than that in bath B or C. Hence again we cannot find a consistent correlation between Cu^{2+} mobility and the copper current efficiency.

From the results of diffusion coefficient and ionic mobility study, we reason that Eq.(4) cannot be the controlling step.

Polarization data for baths A, B and C are shown in Fig.8. They follow the Tafel's Equation. Hence the values of transfer coefficient (α_c) for cathodic reaction, the exchange current density (i_o) for the transfer process, the surface diffusion flux at the reversible potential (v_o) and the Tafel slope (b) can be computed and are shown in Table 5.

TABLE 5

Parameters for copper deposition for different baths.

plating system	i_o (ma/cm^2)	b (mv/decade)	α_c	zFv_o (ma/cm^2, i= 1 ma/cm^2)
bath A	6.03	114.7	0.51	6.21
bath B	3.14	102.7	0.58	6.72
bath C	2.39	106.4	0.55	2.92

The values of i_o, α_c and b are of the same order of magnitude as that reported by Bockris [25][30]. The value of v_o which can be calculated from the steady state value (at low current density) according to Eq.(9) by Bockris' method [25][30].

$$\eta_\infty = RTi/zF(1/i_o + 1/zFv_o) \qquad (9)$$

The total overpotential η_∞ can be divided into five sections [31], ohmic (η_Ω), concentration (η_c), activation ($\eta_{trans.}$), crystallization ($\eta_{surf.diff.}$) and inhibiting(η_i) overpotentials.

$$\eta_\infty = \eta_\Omega + \eta_c + \eta_{trans.} + \eta_{surf.diff.} + \eta_i \qquad (10)$$

At low current density, η_c, η_i are neglected and η_Ω is subtracted from the overpotential measurement. Therefore, Eq.(10) can be rewritten as:

$$\eta_\infty = \eta_{trans.} + \eta_{surf.diff.} \qquad (11)$$

Comparing Eq.(11) with (9), we obtain

$$\eta_{trans.} = RTi/zFi_o \qquad (12)$$

and

$$\eta_{surf.diff.} = RTi/(zF)^2 v_o \qquad (13)$$

Hence,

$$\eta_{\infty}/\eta_{trans.} = 1 + i_o/zFv_o \qquad (14)$$

The ratio of $\eta_{\infty}/\eta_{trans.}$ in Eq.(14) decides which step is the rate determining step of the copper deposition. If $\eta_{trans.} >> \eta_{surf.diff.}$, then the process is determined by the charge transfer step. Otherwise, it is determined by the surface diffusion step. The ratio of i_o to zFv_o and overpotentials for the first three baths in Table 1 with a current density of 1 ma/cm^2 are shown in Table 6.

TABLE 6

Overpotential and i_o/zFv_o ratio of different plating baths at i = 1 ma/cm^2

plating system	$\eta_{trans.}$ (mv)	$\eta_{surf.diff.}$ (mv)	i_o/zFv_o
bath A	1.97	1.91	0.97
bath B	3.75	1.75	0.47
bath C	4.95	4.05	0.82

From Table 6, we can see that only in bath B, i.e. acidic copper sulfate bath, $\eta_{trans.}$ is far larger than $\eta_{surf.diff.}$ and it indicates that the charge transfer step is the only rate determining step. However in other baths, the surface diffusion definitely has great influence on the rate of the deposition process. The above analysis is valid only in systems at low current density. At high current density, the system should be controlled by the charge transfer step according to Bockris' study [23].

The charge transfer of Cu^{2+} is further considered to be a two-step reaction with Eq.(5) being the rate determining step. Therefore, any anions or other ligands present in the electrolyte which can complex with Cu^+ and prevent disproportionation of Cu^+ according to Eq.(3) should theoretically increase the current efficiency. Halide ions can coordinate with Cu^+ ion and the coordination is almost invariably tetrahedral [32]. There is an empirical equation to calculate the formation constant of fluoro - complex cations as follows [33]:

$$\log Q = -0.46 - 1.1\ Y + 0.48\ Z^2/r_+ \qquad (15)$$

where Q is the formation constant for the reaction, Y is the coordination number, Z_+ and r_+ are the charge and radius of the cation. If the coordination number Y is from 1 to 6, and $Z_+=1$, r_{Cu} =0.96 Å [34], we can calculate the formation constant of Eq.(16) to be 8.71×10^{-2}, 6.92×10^{-3}, 5.50×10^{-4}, 4.37×10^{-5}, 3.47×10^{-6} and 2.75×10^{-7} respectively according to Eq.(15).

$$Cu^+ + n\ F^- \rightleftharpoons CuF_n^{1-n} \quad , \text{ for } n = 1 \text{ to } 6 \qquad (16)$$

Therefore, fluoride ions may complex with Cu^+ ion according to Eq.(16) and stabilize it, whereby resulting in an increase of current efficiency.

We then chose a cupric perchlorate bath as the plating electrolyte (bath E in Table 1) and compared its current efficiency with the acid copper sulfate electrolyte (bath D). Both perchlorate and sulfate ions [32] do not complex with Cu^+ and these two ions have the same structure. If our reasoning is correct, we would observe that these two electrolytes have similar current efficiency response with respect to off-time or pulsating current density.

Current efficiencies of baths D and E as functions of off-time and pulsating current density are shown in Figs.9 and 10. From these figures , we find that the current efficiency of bath E is actually slightly lower than that of bath D. This is in striking contrast to results shown in Figs. 2, 3, 4 and 5, in which the baths containing fluorides show considerable higher current efficiency than the pure acid copper bath. Therefore, the result of the perchlorate bath further supports our explanation based on the fluoride ion complex concept.

Our findings and reasoning also support the validity of Eqs.(1) to (3) as the copper deposition model under pulsed current condition.

CONCLUSION

In the pulse plating of three different copper baths (A, B and C), we found that the fluoride-containing electrolytes have higher current efficiency than the acidic copper sulfate solution. The difference is dependent on the length of the off-time or the current density.

A mechanism that involves a two-step charge transfer reaction and a disproportionation of Cu^+ was adopted to explain the experimental data. We propose that Cu^+ can be stabilized by complexation with F^- ion, which slows the Cu^+ disproportionation reaction. Therefore, fluoride-containing electrolytes have higher current efficiency than the acidic copper sulfate electrolyte under pulsed current condition and fluoride ions are a beneficial additive in this process.

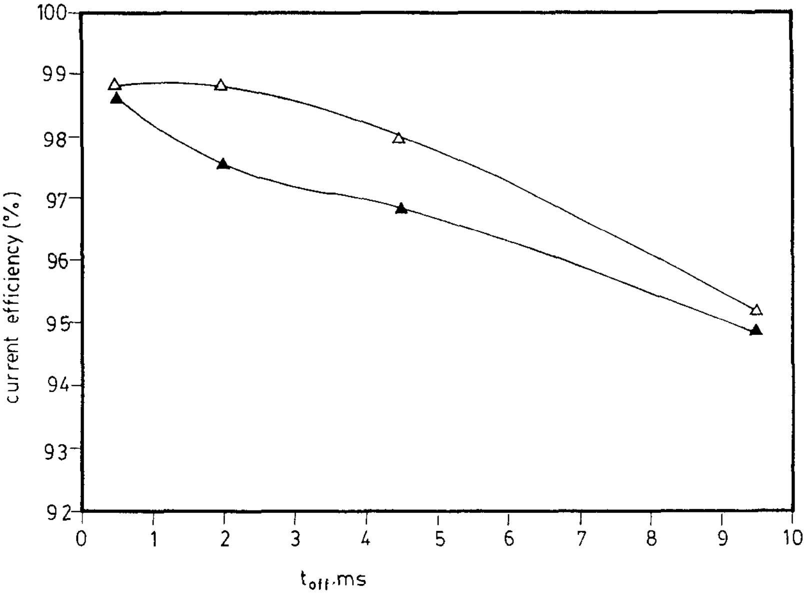

Fig. 9. Cathodic current efficiency versus t_{off} with a constant t_{on} (0.5 ms) and a constant pulse current density (81.96 ma/cm^2). △: bath D, ▲: bath E.

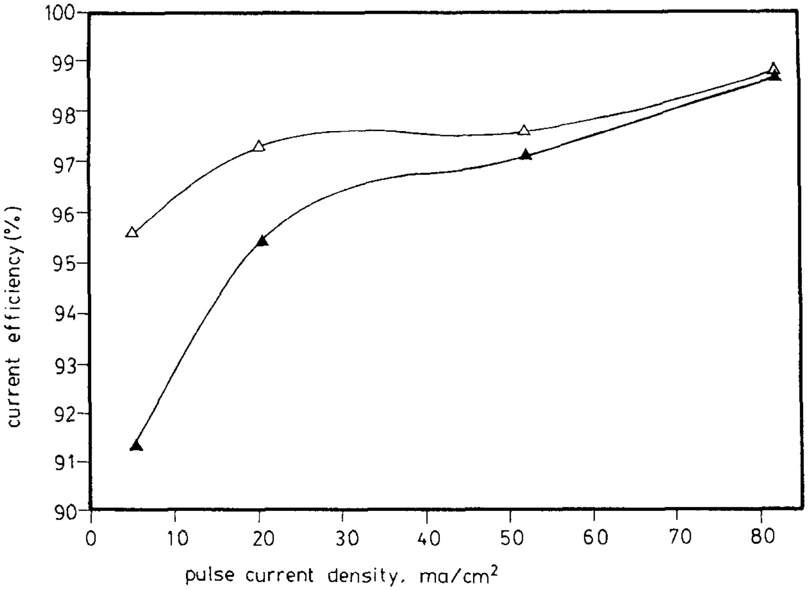

Fig.10. Cathodic current efficiency versus pulse current density with a constant t_{on} (0.5 ms) and a constant t_{off} (0.5 ms). △: bath D, ▲: bath E.

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