A Study of the Current Efficiency Decrease Accompanying Short Pulse Time for Pulse Plating

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ABSTRACT

This investigation is concerned with the variation of current efficiency under pulse current conditions. The parameters involve the pulse current density, the on-time, and the off-time. When the on-time is shorter than a critical pulse time, the efficiency drops noticeably. A model based on successive charge transfer steps and a side reaction is proposed to explain the experimental observations.

Pulse plating, with its several process parameters and higher instantaneous current density than for direct current plating, has received attention in recent years (1-11) and proved to be an important technology for improving the properties of deposits (12-20). Two advantages are cited by investigators in the field. First, a higher average cathodic current density for deposition can be applied to the plating system. Although the theoretical limiting current density may be a constant either under dc or pulse plating (1), the practical current limit for pulse current could be much higher than for dc plating (17). Second, a fine-grained deposit can be obtained. Adjustment of on-time (t_{on}), off-time (t_{off}), and current density of the pulse current, can lead to the desired properties.

In addition to its influence on deposit properties, the effect of the pulse plating on current efficiency is another important research area. Wan *et al* (21) found that the cathodic current efficiency of the pulse plating of the copper in a copper sulfate solution drops from nearly 100% (t_{on} = 1s) to values ranging from 80.4 to 93.7% when current is pulsed in the millisecond range. A mathematical model (22) was formulated to explain this behavior of a $Cu/CuSO_4$ system under pulsed current conditions on a rotating disk electrode. This model includes a two-step reduction with different reaction rates during the on-time and a disproportionation of cuprous ions to form copper and cupric ions. This model, however, fails to explain the current efficiency reduction in systems where such a disproportionation of a partially discharged intermediate is unlikely. One such system is the deposition of Pb in lead fluoroborate bath.

Puippe and Ibl (23) postulated a model to describe the mass transport and the double layer effect in pulse plating. The model involves charging of the double layer during the on-time and discharging during the off-time. In theory, the double layer effect should not affect the current efficiency.

Hosokawa *et al.* (24) concluded that the current efficiency for pulse plating of rhenium exhibits a sharp drop as the on-time is decreased below a threshold value, in the range of 0.5-0.005 ms. Eckier *et al.* (25) also found that for the pulse plating of molybdenum and chromium-molybdenum, the current efficiency has a maximum with respect to the balance between on-time and off-time. Hosokawa *et al.*'s research (17) on the pulse plating of zinc again shows a current efficiency maximum at 0.5 ms t_{on}. For the electrodeposition of silver by pulse current in cyanide solution, Hosokawa and co-workers (26) determined the optimal t_{on} with respect to current efficiency for different current densities. Yoshimura *et al.* (27) studied the pulsed plating of palladium and found that the current efficiency decreases when t_{on} drops below 0.5 ms. On the other hand, Miu and Fung (28) found that in rhodium pulsed plating the efficiency increases with decreasing t_{on}.

From this discussion, we understand that the current efficiency in most cases shows a noticeable decrease for very short current pulsing. Hence, pulse plating, although it shows many property improvements over dc plating, deserves a more careful study of its current efficiency. In this paper, we consider the change of the current efficiency in acidic copper and fluoroborate tin, lead, and lead-tin systems and provide a mechanism to explain the result.

Experimental

A rectangular Lucite cell (10 × 10 × 5 cm) was used for the plating. Copper panels with fcc crystallites were used as the cathode; lead-tin alloy, Pb, Sn, and Cu plates were used as the anodes for solder plating, lead plating, tin plating, and copper plating, respectively. All the chemicals used were reagent grade. The plating bath compositions are recorded in Table I.

Plating was carried out at room temperature (20°-30°C) with magnetic stirring at 300 rpm. All plating experiments were run under constant current. The pulse current waveform was generated by a direct current power supply which was controlled through an interface (AD500A programmable multifunction unit) by a microcomputer. A Hitachi VC-6020 digital storage oscilloscope was used to measure the current response.

The current efficiency was calculated by weighing the deposit and converting to a coulomb equivalent. The total coulombs passed value was calculated by: (*i*) measuring the on-time, off-time, and the pulsating current for one cycle by means of an oscilloscope, then (*ii*) recording the number of cycles using the counter, which is a functional card installed in the AD500A. According to the data and the weight increase of the cathode, we can calculate the current efficiency exactly. The corrosion rate of the metal deposition (R_{loss}) during the plating was also measured by immersing a metal piece in the plating bath and measuring the weight loss. The corrosion loss has to be taken into consideration to give a more accurate measure of the plating current efficiency.

The deposit structures under various plating conditions were characterized by x-ray diffraction with a Cu-Kα source, and the surface morphology of the deposit was recorded with a scanning electron microscope (SEM).

Results and Discussion

Current efficiency as a function of t_{on} and current density.—Because the character of the electrodeposit can be influenced by the deposit's thickness (29), we held this parameter at 0.02 mm except for the experiments summarized in Fig. 1 in which the thickness is 0.8 mm.

The dependence of the current efficiency (*CE*) of a Pb/Sn system, with a fixed duty cycle, on both pulse current den-

Table I. Compositions of the plating baths

Constituent	Concentration (*M*)			
	Bath A	Bath B	Bath C	Bath D
$Pb(BF_4)_2$	0.051	—	0.051	—
$Sn(BF_4)_2$	0.205	0.205	—	—
$CuSO_4$	—	—	—	0.75
HBF_4	1.00	1.00	1.00	—
H_2SO_4	—	—	—	1.00
Starter (ml/liter)[a]	70	70	70	—

[a] EC848, Electronic Chemical, Incorporated.

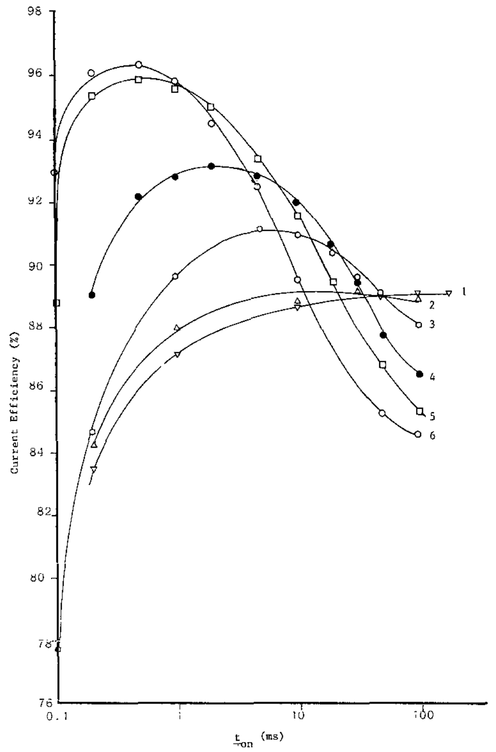

Fig. 1. Influence of pulse length (t_{on}) on current efficiency of Pb/Sn deposition at different pulse current density (I_p) with duty cycle = 25%. The pulse current densities are: curve 1:0.54, curve 2:2.15, curve 3:4.31, curve 4:8.61, curve 5:17.22, curve 6:34.44 A/dm^2.

sity and t_{on} is shown in Fig. 1. As t_{on} decreases from 100 to 0.1 ms, there is always a maximum *CE* for every current density. When the pulse current density increases from 0.215 to 34.44 A/dm^2, the on-time for the maximum *CE* decreases from 100 to 0.3 ms and the value of the maximum *CE* increases from 89 to 96.4%. From Fig. 1, we can conclude that there is an optimal t_{on} with respect to current efficiency for every current density. And this optimal t_{on} decreases as we increase the applied current.

Similar results can also be observed for other plating systems, as shown in Fig. 2. Here, plating systems were tested with a much smaller current density than used for the experiment reported in Fig. 1. Besides the Pb/Sn system, pure lead, tin, and copper depositions were also studied. From Fig. 2, we conclude that the current efficiency for deposition of the acidic copper plating system drops sharply when the t_{on} is smaller than 5 ms. This phenomenon has been investigated by Wan *et al.* (21). They propose a disproportionation reaction to explain the *CE* reduction. This model might also be applicable to the tin plating system, but it fails to account for the behavior of the lead plating system since the lead ions do not form monovalent ions which can undergo disproportionation. An optimum pulse length with respect to *CE* has also been found in silver plating by Hosokawa *et al.* (26). We therefore conclude that the *CE* drop as t_{on} reaches very small values is a general phenomenon and disproportionation of partially discharged intermediate cannot fully explain the results.

For comparison, we also studied the efficiency under direct current for different plating baths. According to Fig. 3, we find that in most acidic plating systems, the current efficiency typically exceeds 90. However, when the current is raised to a certain value, *e.g.*, exceeding 0.5 A/dm^2 in the pure Pb case, the surface concentration of the active ions drops significantly and causes a side reaction such as hydrogen evolution to occur. This is fairly common in most plating applications. However, when the current density is very small, *e.g.*, 0.1 A/dm^2 in the pure lead plating system, the current efficiency would also decrease. This phenomenon is rarely mentioned in the literature and certainly cannot be explained in terms of concentration polarization. We suspect that there is some relationship between the existence of *CE* maximum in pulse plating (Fig. 2) and the existence of *CE* maximum in dc plating.

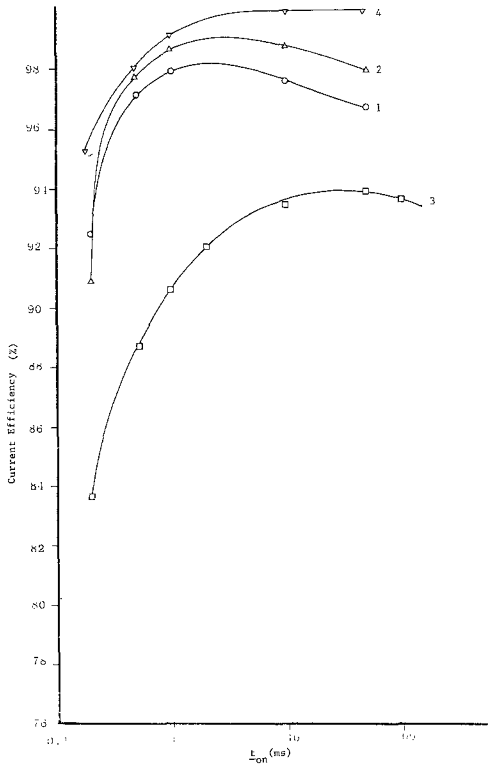

Fig. 2. Influence of pulse length (t_{on}) on current efficiency at different plating systems with the pulsating current density (I_p) = 0.54 A/dm^2 and duty cycle = 25%. The systems are curve 1, Pb/Sn; curve 2, Pb; curve 3, Sn; curve 4, Cu (H_2SO_4).

The similar *CE* reduction either in a long t_{on} of pulse plating system or a high current density of dc plating system is quite obvious. Both represent a depletion of active ions near the surface which causes a decrease of the current efficiency. But in the other extreme, where we also observe a decrease of the *CE* for very short t_{on} of pulse plating or very low current density of dc plating, a more complex explanation is needed. Figures 4 and 5 show the variation of *CE* at various pulse current densities for two different t_{on} values. It is obvious that the effect of t_{on} is more pronounced than that of the pulse current density. For instance, in the copper plating system, the *CE* drops from 99 to 80% as the pulse current density decreases from 1.0 to 0.1 A/dm^2 for a t_{on} of 50 ms, but the current efficiency drops from 94 to 20% for a t_{on} of 1 ms. In the following discussion, we determined the effects of the current density and then the on-time individually.

First, we suspect that metal corrosion could be the major cause of *CE* reduction. We define a rate of the deposit loss, R_{loss}, to be equal to the difference between the ideal rate at 100% current efficiency and the actual deposit rate

$$R_{loss} = R\,(100\%\ CE) - R\,(\text{actual}) \qquad [1]$$

where the units of *R* are mol/h for a given electrode surface. We measured the corrosion rate of the deposit and the

Table II. The rate of corrosion (R_{corr}) and weight loss (R_{loss}) (10^{-6} mol/h)

		Pb/Sn	Sn	Pb	CuSO$_4$
R_{loss}: DC	0.1034[a]	7.8	97.2	17.4	15.5
R_{loss}: P.C. (t_{on} (ms))					
P.C. (50)	0.0108[a]	18.2	102.1	25.6	22.5
P.C. (1)	0.0430	39.1	148.6	61.7	35.8
P.C. (1)	0.1211	35.4	140.1	47.4	28.8
P.C. (0.2)	0.1181	105.9	230.4	115.3	66.1
P.C. (0.1)	0.1205	181.2	327.9	183.2	99.7

[a] Average current density (A/dm^2)

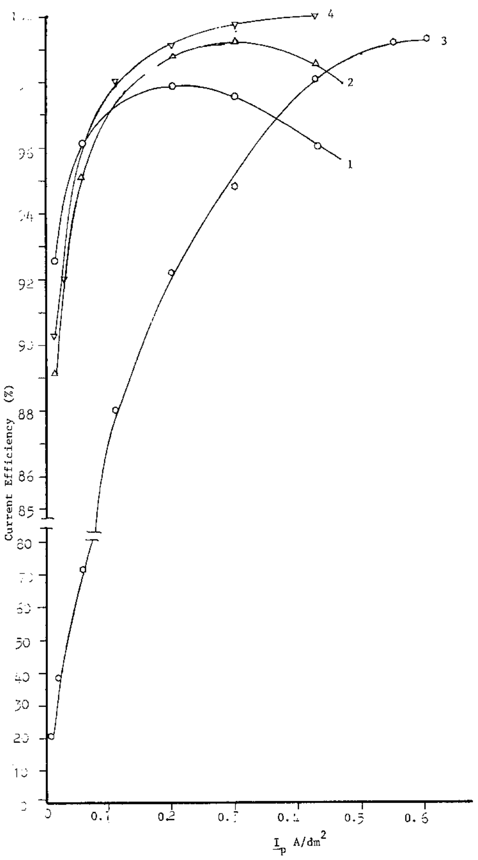

Fig. 3. Influence of current density on current efficiency at different plating systems with the direct current. The systems are curve 1, Pb/Sn; curve 2, Pb; curve 3, Sn; curve 4, Cu (H_2SO_4).

R_{loss}. From the results in Table II, we find that the corrosion reaction is slow relative to the R_{loss}, and it cannot be the main cause for the *CE* drop. For instance, in Sn plating, the corrosion rate is 11.9×10^{-6} mol/h. But the R_{loss} for dc plating is 97.2×10^{-6} mol/h at 0.0134 A/dm² and 148.6×10^{-6} mol-h for a pulse plating with a t_{on} of 1 ms and current density of 0.043 A/dm². In addition, as the t_{on} is shortened, the R_{loss} increases pronouncedly. This phenomenon indicates that there must be another side reaction besides the corrosion.

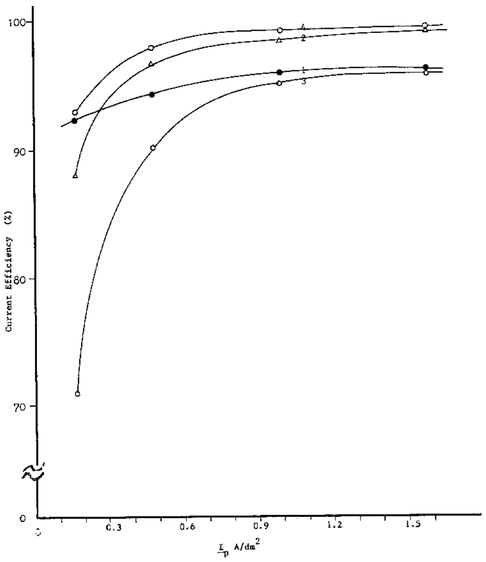

Fig. 4. Influence of pulse current density (I_p) on current efficiency at different plating systems with pulse length (t_{on}) = 50 ms and duty cycle = 25%. The systems are curve 1, Pb/Sn; curve 2, Pb; curve 3, Sn; curve 4, Cu (H_2SO_4).

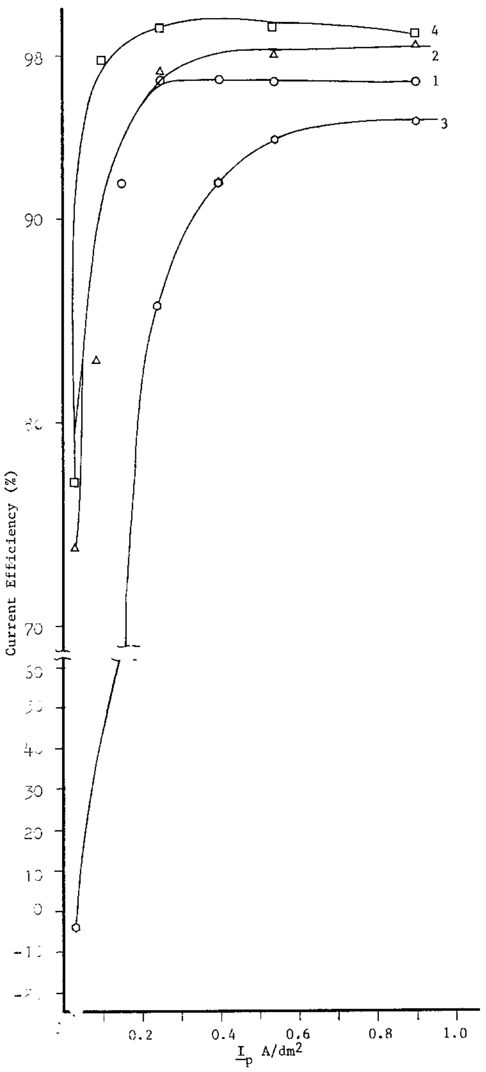

Fig. 5. Influence of pulse current density (I_p) on current efficiency at different plating systems with pulse length (t_{on}) = 1 ms and duty cycle = 25%. The systems are curve 1, Pb/Sn; curve 2, Pb; curve 3, Sn; curve 4, Cu (H_2SO_4).

Reaction mechanism.—Therefore, we postulate a mechanism as follows

$M^{+2}_{(aq)} \longrightarrow M^{+2}_{(ad)}$ adsorption [2]
$M^{+2}_{(ad)} \longrightarrow M^{a}_{(ad)}$ charge transfer [3]
$M^{+2}_{(ad)} \longrightarrow M^{+1}_{(ad)}$ intermediate formation [3a]
$M^{+1}_{(ad)} \longrightarrow M^{a}_{(ad)}$ charge transfer [3b]
$M^{*}_{(ad)} \longrightarrow M_{(cry)}$ surface diffusion [4]
$M^{*}_{(ad)} \longrightarrow M$ metal degradation [5]
$M^{+1}_{(ad)} \longrightarrow M^{+2}_{(aq)} + M_{(s)}$ disproportionation [6]

where reaction [3] is the two-electron charge transfer and [3a] and [3b] are two successive one-electron charge transfer steps with a monovalent cation as the intermediate. Reactions [3a] and [3b] are alternatives to reaction [3] when there exists a stable monovalent intermediate such as Cu^{+1}. Reaction [4] is the surface diffusion of discharged atoms (adatoms) into crystal lattice. Reaction [5] is a side reaction in which the adatom fails to be incorporated into the crystal and reenters the electrolyte. We call it "degradation" and it competes with reaction [4]. This reaction has also been mentioned by Hibert (30). A more detailed discussion of this reaction will be presented in the next section. The degradation and other side reactions such as hydrogen evolution will reduce the *CE*. Conway and Bockris (31) studied the deposition of copper and concluded that adatoms are partially hydrated. They indicated that surface diffusion is the rate-determining step at low current density, while charge transfer tends to be the rate-determining step at higher cathodic potential. We considered

Table III. Current efficiency (%) for dc and pulse current modes

Mode	CD (A/dm^2)	Composition Pb/Sn	Sn	Pb	CuSO$_4$
DC	0.0134	95.51	39.20	89.10	90.27
	0.0594	96.14	72.61	95.13	91.96
	0.1209	97.36	88.06	97.73	98.12
	0.4305	96.03	98.09	99.53	100.0
P.C. 50[a]	0.0108	81.43	− 4.34	73.82	77.05
	0.0578	96.83	73.54	92.95	97.96
	0.1268	96.74	93.96	97.96	99.50
	0.2377	95.62	94.69	98.54	98.87
P.C. 1	0.0430	92.32	71.03	87.98	93.03
	0.1211	94.32	90.31	96.72	98.01
	0.3938	96.18	95.83	99.19	99.15
P.C. .2	0.1181	92.49	83.66	91.84	95.31
P.C. .1	0.1205	80.81	56.57	74.36	75.15

[a] Pulse current with duty cycle = 25% and the number is the on-time (ms) and the value of CD is the average CD.

that the adatoms are high energy units before they diffuse to steps and to kink sites where they are incorporated. These adatoms are naturally more active than the atoms in the crystal. They may undergo degradation and cause a reduction of *CE*. The rate of this degradation is determined by the concentration of the adatom $[M_{(ad)}]$. When the current density is low, the surface diffusion is the rate-determining step and the degradation of the adatom is competing with the surface diffusion. But at high current density, the charge transfer becomes the rate-determining step. The surface diffusion of the adatom is then relatively quite fast, which reduces the concentration of the adatom and makes the rate of the degradation negligible. This degradation of adatoms is the reason that in dc plating, when the current density is very small, we observe a drop of *CE*. And when we raise the current density, the *CE* also goes up until the current density is so high that concentration polarization becomes significant and other side reactions make the *CE* drop again.

For pulse plating, we shall show that for very short pulses, there is an initial unstable period, during which the cathodic activation overpotential is not fully developed even for high current processes. This unstable transition period favors the degradation of the adatom in the same manner as does a low current density, weakly polarized dc plating system. This is the reason that when we reduce the t_{on} in the millisecond range, we also observe a drop of *CE* as reported in Table III. For instance, in the Sn system at a current density of about 0.012 A/dm^2, when the t_{on} is reduced from 50 to 1 ms and finally to 0.1 ms, the *CE* decreases from 93.96 to 90.31% and finally to 56.57%. For acidic tin and copper systems, both reactions [5] and [6] are causes for *CE* reduction. But for the lead system, degradation is the only main reaction responsible for *CE* reduction.

Waveform of pulse and underpotential deposition.—In order to learn more about the t_{on} effect, we recorded the cathodic overpotential response with an oscilloscope (Fig. 6). There is a transition period (t_{trans}) in the initial region of the pulse before the activation overpotential rises to the steady state. This transition time is about 0.18 ms with a 17.22 A/dm^2 pulse current density. We also found that the transition time is independent of the duration of t_{on} at a certain duty cycle or pulse current density. Hence, when the t_{on} is shortened, this transition period becomes relatively more significant. In our case, if the t_{on} is less than 0.18 ms, the activation overpotential actually never reaches the steady state. This transition period has nothing to do with the double layer. Ibl (32) indicated that the number of coulombs of the double layer discharge is exactly equal to that of the charge. Therefore it should not affect the faradic current efficiency. Puippe and Ibl (23) postulated that the charge time (t_c) and the discharge time (t_d) are dependent on the pulse current density only, and we estimated the t_c and t_d to be

$$t_c = 1700/I_p \qquad [7]$$

$$t_d = 12{,}000/I_p \qquad [8]$$

where t_c and t_d are the charge time and discharge time in microseconds and I_p is the pulse current density in A/dm^2. In our case, in a Pb/Sn system with an I_p at 34.44 A/dm^2, the t_c would be 0.04 ms according to Eq. [7]. However, the t_{trans} was measured to be 0.15 ms. This again shows that the transition response is not a result of the double layer charging. Hence we postulate that the reason for the easy occurrence of degradation during this transition period is that the deposition proceeds via underpotential deposition (UPD).

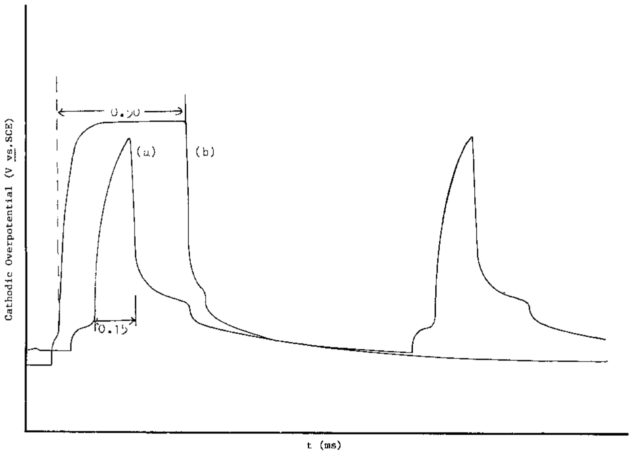

Fig. 6. The cathodic overpotential diagram of Pb/Sn system at different pulse length (t_{on}) with pulse current density (I_p) = 17.22 A/dm^2 and duty cycle = 25%. The values of t_{on} (ms) are: (a) 0.15, (b) 0.50.

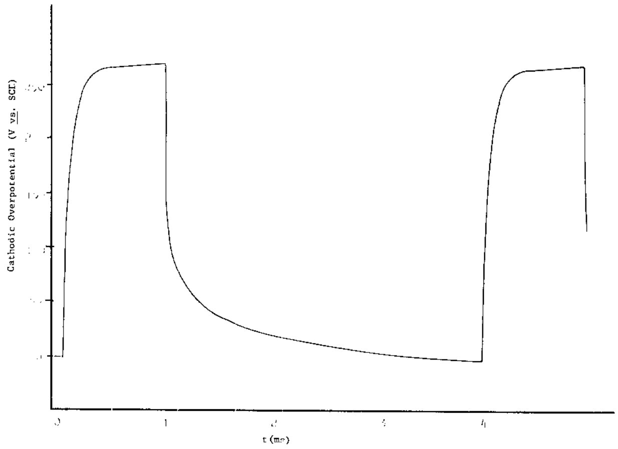

Fig. 7. The cathodic overpotential diagram under the pulse current with I_p = 8.61, t_{on} = 1 ms, and duty cycle = 25%.

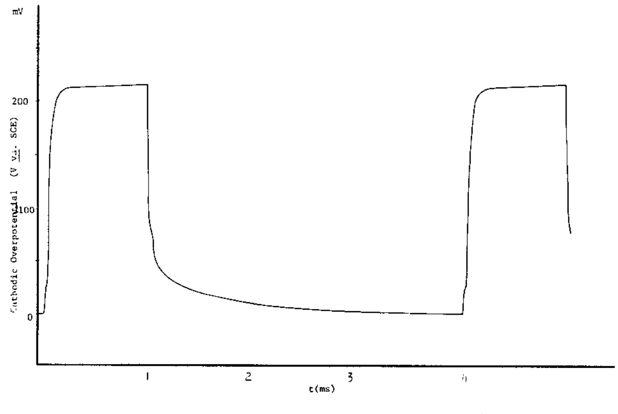

Fig. 8. The cathodic overpotential diagram under the pulse current with I_p = 16.22, t_{on} = 1 ms, and duty cycle = 25%.

UPD is electrodeposition onto solid electrodes at potentials more positive than the reversible potential (33-38). Under this condition, the reactants are adsorbed onto the electrode surface and then discharged to adatoms which obtain a two-dimensional atomic array. Since the atoms have not reached the stable, fully crystallized stage in the transient time, they are easily dissolved if the current is interrupted such as in a pulse plating with very short pulse. We reason that in the transition period of the pulse when the potential is much lower than the steady-state potential, the deposition proceeds via UPD or a process at least similar to UPD with the freshly deposited adatoms being quite unstable and prone to degradation. When we lengthen the t_{on}, a major portion of the pulse would be in the steady state and the transition period becomes relatively insignificant as shown in Fig. 6b. This consequently causes a rise of the current efficiency. But if we further lengthen the t_{on} or increase the current density, we may push the system into noticeable concentration polarization and induce other side reactions. This competition results in the rise and fall of current efficiency with respect to pulse length and current density.

A comparison between Fig. 7 and 8 also shows that the transition duration is dependent on the pulse current density only and independent of t_{on}. When we reduce the pulse current density from 17.22 (Fig. 8) to 8.6 A/dm^2 (Fig. 7), the transition duration increases from 0.18 to 0.26 ms. Therefore a lowering of current density works similarly to a shortening of t_{on} so as to make the transition period more important and to cause a reduction of *CE*.

Our hypothesis is supported by trends in the morphology and the preferred orientation of the deposit by pulse plating and by the detection of suspended particles in the solution of the plating system. We observed the morphology of the deposit by scanning electron microscope (SEM) as the t_{on} is shortened from 5 to 0.2 ms (Fig. 9). It is obvious that the surface morphology of the deposit becomes smoother and forms a fine-grained deposit as the t_{on} is decreased from 5 to 1 ms. But when the t_{on} is less than 0.5 ms, a different morphology forms. The morphology becomes needle-shaped to mossy with t_{on} being decreased from 0.5 to 0.2 ms. Since the transition period is about 0.26 ms, our finding is consistent with the UPD two-dimensional array theory.

We then studied the orientation transformation of the deposit by x-ray diffraction. We have shown in a previous paper (29) that the preferred orientation of the lead in the lead/tin deposit is determined by the substrate, the deposit thickness, the limiting current density, and the pulse current conditions, involving t_{on}, t_{off}, and I_p. There we defined a ratio, R

$$R = T_{111}/T_{200} \qquad [10]$$

where T_{111} and T_{200} are the intensities of the texture <111> and <200> of the lead in the lead/tin deposit. The variation of R *vs.* t_{on} is shown in Fig. 10. It is obvious that the ratio R decreases with the shortening of the t_{on}. This result reveals that at the transition state, the texture <200> becomes the preferred orientation. We understand that the <111> plane grows in a three-dimensional fashion while the <200> plane grows in two dimensions (39). Therefore, the <200> dominance in the very short pulse system is also consistent with our UPD reasoning. Similar results were observed by Fukumoto *et al.* (40) in the deposit of the Pd/Ni alloy under pulse current.

Finally, we found that the Pb, Sn, and Pb/Sn alloy plating systems are all stable throughout the 120h working time when t_{on} is over 1 ms, but they become unstable and generate observable suspensions in less than 48h working time with a 0.2 ms t_{on}. The suspension was dissolved in hy-

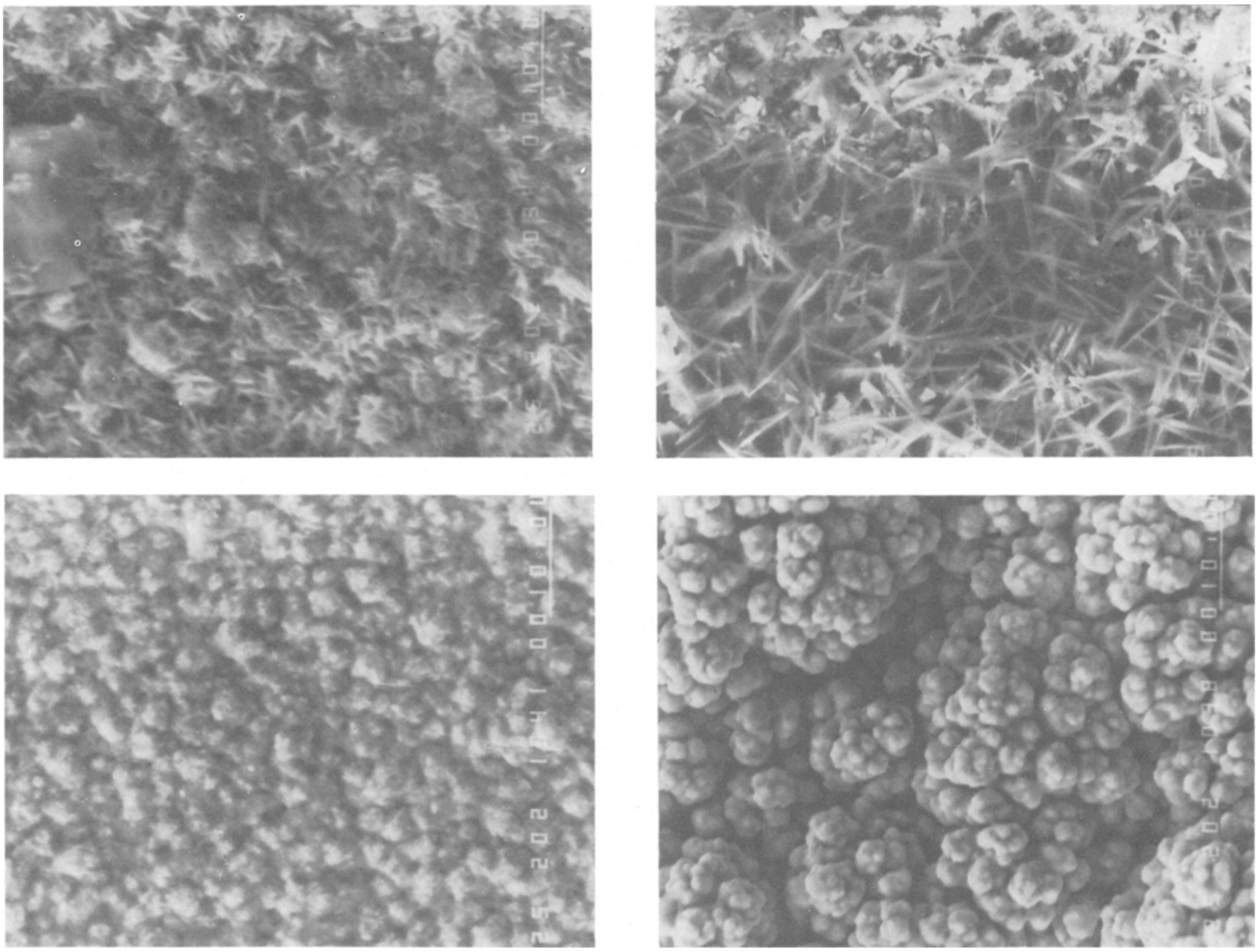

Fig. 9. Influence of pulse length (t_{on}) on the morphology of the deposit of the Pb/Sn alloy with pulse current density (I_p) = 34.44 A/dm^2 and period ($T = t_{on} + t_{off}$) = 50 ms. The values of t_{on} (ms) are (a, top left) 0.2; (b, top right) 0.5; (c, bottom left) 1.0; (d, bottom right) 2.0.

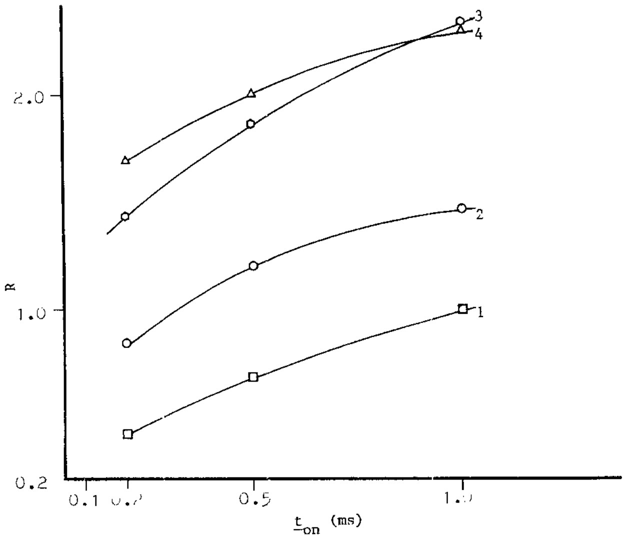

Fig. 10. Predomination of the lead in the lead-tin alloy as a function of the on-time with pulse current density (I_p) = 34.44 A/dm^2 and duty cycle = 25%.

drofluoric acid and was identified to be a mixture of leadoxide and tin-oxide for the Pb/Sn system and PbO for the lead system. This again supports the existence of metal degradation in very short pulse and explains the outcome of that reaction.

Conclusion

In the pulse plating of acidic Sn/Pb, Sn, Pb, and Cu systems, we found significant *CE* lowering. The degree of *CE* reduction is dependent on the t_{on} length or current density and the nature of the plating bath.

A mechanism that involves a charge transfer reaction, competition between the surface diffusion, and the degradation of the adatom and a disproportionation of monovalent ion was proposed to explain the phenomenon. In the initial region of the pulse, there is a transition state. We considered that the deposition reaction proceeds partially as a UPD reaction in this period. The morphology and the preferred orientation of the deposit support our hypothesis. The suspension indicated that in very short t_{on}, the deposit of the transition period is active and easily reoxidized.

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LIST OF SYMBOLS

CE	current efficiency (%)
I_p	pulse current density
M*	an adatom; this exists as an intermediate between the discharge and the crystal growth
R	ratio of the intensities of the texture <111> to <200>
R_{loss}	the difference between the ideal deposit rate and the real rate with unit mol/h
T	the length of the period of the pulse
T_{111}	the intensity of the texture <111> of the lead in the lead-tin alloy which was measured by x-diffraction
T_{200}	the intensity of the texture <200> of the lead in the lead-tin alloy which was measured by x-diffraction
t_c	charge time of the double layer in μs
t_d	discharge time of the double layer in μs
t_{on}	on-time of the pulse current
t_{off}	off-time of the pulse current
t_{trans}	the transient time before the activation overpotential goes to the steady state

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