Effect of pulse plating on composition of Sn–Pb coatings deposited in fluoroborate solutions

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Abstract

Galvanostatic pulsed current (PC) and pulse reverse (PR) plating of Sn–Pb coatings onto copper rotating disks from fluoroborate solutions has been conducted to obtain alloy compositions otherwise not achievable by DC plating. PC plating investigated over a wide range of pulse frequencies (20 Hz–200 kHz) and duty cycles produces coatings with compositions that differ only slightly from those obtained by DC plating at the same current density. On the other hand, the use of PR plating can be dramatic, producing Pb contents both well above and below that achievable by DC plating. Varying the frequency from 20 Hz to 200 kHz with the duty cycle and average current density fixed at 80% and 3.78 A dm^{-2} yields compositions between 2.5 and 28 wt.% Pb. The Pb:Sn ratio in the deposit is always lower than that in the plating bath when a PR frequency of 20 Hz is imposed, but generally exceeds it at a frequency of 20 kHz. Alloy composition appears to be closely related to the working electrode potential reached during the anodic pulse. A higher frequency leads to less positive potentials during the anodic pulse and shorter anodic pulse times, which may enhance Sn dissolution and enrich the coating in Pb.

1. Introduction

There has been considerable interest in the electrodeposition kinetics and properties of Sn–Pb coatings due to their importance to the electronics industry [1–8]. One of the first investigations on kinetics was conducted by Cheng and Cheh [9] on the galvanostatic pulsed current (PC) plating of tin, lead and tin–lead alloys onto a rotating disk electrode in fluoroborate solutions. Assuming that Sn and Pb deposition occur independently of one another, Cheng and Cheh presented a model that predicted the observed current–potential behaviour and alloy compositions reasonably well. This model was extended by Pesco and Cheh [10] to incorporate 2-dimensional transport and migrational effects and compared with experimental radial profiles of deposit content and total current for DC plating. Good agreement was obtained when the plating bath was additive-free. However, less than satisfactory results were obtained when the surfactant Triton X-100 was present due to a significant increase in cathodic polarization, presumably due to interactions between the organic and the metal ions. Tam [11] investigated Sn–Pb deposition onto a rotating disk electrode in fluoroborate solutions containing peptone and also reported evidence of substantial interactions between the metal ions and the adsorbed organic.

Chen et al. [12] studied alloy electrodeposition from methane sulphonate acid solutions containing equimolar Pb^{2+} and Sn^{2+} concentrations in the absence of organic additives and reported that the deposition of each metal occurs independently of the other in both kinetic- and mass transfer-controlled regimes. In these solutions, the resulting alloy contained more Pb than Sn due to faster electrode kinetics and mass transfer.

DC plating in methane sulphonate baths was also studied by Kim et al. [13]. They found that the Pb content in the alloys rose sharply to the desired 20 wt.% with increase in applied current density to approximately 3 A dm^{-2} and thereafter remained unchanged at higher current. The addition of an organic grain refiner substantially increased the cathodic polarization during deposition and led to a much finer-grained deposit.

Recent studies on Sn–Pb deposition were conducted by Petersson and Ahlberg [14, 15] on glassy carbon and polycrystalline gold electrodes in fluoroborate solutions in the absence of organic additives. They found that the alloy deposition rate is controlled by metal ion diffusion to the electrode surface with 3-dimensional growth of metal nuclei.

Few pulse plating studies of the Sn–Pb system have been reported. In addition to the work of Cheng and Cheh [9], Kim et al. [13] investigated PC plating in methane sulphonate acid solutions. Variation of frequency and duty cycle from 10 to 100 Hz and 10–80%, respectively, at an average current density of 10 A dm^{-2} had little effect on deposit composition, yielding the same result achieved by DC plating. However, it affected

morphology significantly and produced very fine grains at low frequency and duty cycle that became coarser as duty cycle and frequency increased. Doss [7] compared the application of DC and PC plating to fabricate Sn–Pb studs for use in magnetic recording disk heads and found PC plating to yield more uniform and smooth deposits. No studies on the use of pulse reverse (PR) plating to produce Sn–Pb alloy coatings have been reported. Previous work on other systems (e.g., Ni–Fe, Co–Fe) has shown that the use of PR mode can affect deposit composition differently than that of PC mode [16–18].

This communication reports on the application of both PC and PR modes of electrolysis to produce Sn–Pb coatings in a fluoroborate solution with a Pb:Sn weight ratio of 1:4. The effects of pulse frequency, duty cycle and cathodic pulse amplitude on deposit composition will be described. These results will be discussed in terms of the relative deposition and dissolution rates of the two metals during pulse plating, as inferred from the variation of electrode potential monitored on a digital oscilloscope.

2. Experimental

2.1. *Apparatus*

Plating experiments were conducted at room temperature in a cell with a volume of about 100 ml. A copper disk working electrode was mounted to the end of a rotating disk assembly (Pine Instruments). The counter electrode was a 2×2 cm platinum plate embedded in inert plastic at the bottom of the cell. The working electrode–counter electrode spacing was maintained at 2 cm. To measure the working electrode potential, a saturated calomel electrode was inserted into the cell close to the working electrode. All electrode potentials are reported on the standard calomel scale.

2.2. *Materials*

A standard acidic fluoroborate electroplating bath with a Sn:Pb weight ratio of 4:1 and composition given in Table 1 was used. Reagent grade tin fluoroborate ($Sn(BF_4)_2$), lead fluoroborate ($Pb(BF_4)_2$) and fluoroboric acid (HBF_4) were added as 50 wt.% aqueous solutions (Sigma-Aldrich). Peptone and gelatin were obtained in granular form (Fisher Scientific).

2.3. *Working electrode preparation*

Electrode disks with a 0.64 cm diameter and 0.317 cm^2 exposed area were cut from 99% pure copper. Before

Table 1. Composition of tin–lead electroplating bath used in this study

$Sn(BF_4)_2$	40 g Sn l^{-1}
$Pb(BF_4)_2$	10 g Pb l^{-1}
HBF_4	15 g l^{-1}
Peptone	5 g l^{-1}
Gelatin	2 g l^{-1}

each experiment, a disk was immersed in 1 mol l^{-1} HNO_3 solution for 2 min to dissolve oxidation products and then rinsed in deionized water. Next, it was cleaned for 5 min in ethanol under ultrasonic action, followed by rinsing in deionized water. SiC type abrasive paper (600 grade) was then used to polish the electrode surface. Each disk was rinsed again with deionized water, dried in air and finally weighed.

2.4. *Analysis of deposit composition*

Deposit composition was obtained by immersing a coated disk in a 2 mol l^{-1} HNO_3 solution for 3 min to strip the coating and determining the Pb and Sn content of the resulting solution using direct current plasma (DCP) spectroscopy. The wavelengths used for tin and lead analyses were 284 and 368 nm, respectively.

2.5. *DC plating*

DC plating experiments were conducted over a range of current densities between 0.5 and 20 A dm^{-2} using an EG&G PAR 273 model potentiostat/galvanostat. Current densities above 20 A dm^{-2} were not applied since this would produce coarse deposits. The plating duration was adjusted for each applied current to yield a deposit with a mass of about 0.003 g.

Repeated DC plating runs at 3.78 A dm^{-2} and 500 rpm agitation speed from the same bath showed that 40 successive coatings with essentially the same composition could be produced from an 80 ml batch of electrolyte. It was therefore considered safe to use each bath for 20 plating runs in the subsequent experiments. These results also indicated good reproducibility of the plating procedure and deposit compositional analysis. Statistical analysis of the 40 successive plating runs yielded an average deposit composition and 95% confidence interval of 17.03 ± 0.93 wt.% Pb.

2.6. *Pulse plating*

Galvanostatic PC and PR pulses were applied using a model PR4PARAM rectifier (LWD Scientific). The effects of pulse frequency, duty cycle and current amplitude on the composition of deposits produced by PC and PR plating were examined independently. The parameter ranges investigated were: pulse frequency: 20 Hz–200 kHz, duty cycle: 20–90%, cathodic pulse amplitude: 1.9–15.0 A dm^{-2}.

Obviously, the deposition and dissolution of the two metals during pulse plating and the resulting alloy composition should be closely related to changes in the electrode potential of the copper disk throughout each pulse cycle. To gain some insight on this question, the input current signal and working electrode potential were continuously monitored with a digital oscilloscope (Agilent 54624A) throughout the pulse plating experiments. The electrode responses shown in this paper

correspond to those attained once stationary conditions were reached. The responses obtained at the highest frequencies of 20 and 200 kHz were moderately noisy. Consequently, the results presented for these frequencies were smoothed by taking moving averages of the data. The responses reported at the lower frequencies have not been smoothed.

3. Results and discussion

3.1. *Effect of current density on alloy composition during DC plating*

For comparison purposes, the effect of current density on deposit composition during DC plating was studied using the standard bath. As shown in Figure 1, the Pb content increases with applied current density from 8.2 wt.% Pb to slightly above 18 wt.%. The increase is largest at low current densities and essentially vanishes once the current density rises above 4 A dm^{-2}. These results are consistent with those of Kim et al. [13] for deposition from a methane sulphonate acid solution. They found that the Pb content rose sharply to 21 wt.% as current density increased to 3 A dm^{-2} and thereafter remained constant.

The results in Figure 1 clearly show that Pb deposition is being inhibited. At low current densities, the Pb:Sn weight ratio in the deposit is much lower than the 1:4 ratio in the electrolyte. An increase in current density causes the content of the more noble Pb to rise and eventually level off at 18.1 wt.%, still less than the percentage present in the electrolyte. Evidence for inhibition of Pb deposition in the Sn–Pb system has been reported previously in both fluoroborate and sulphonate solutions [13, 19].
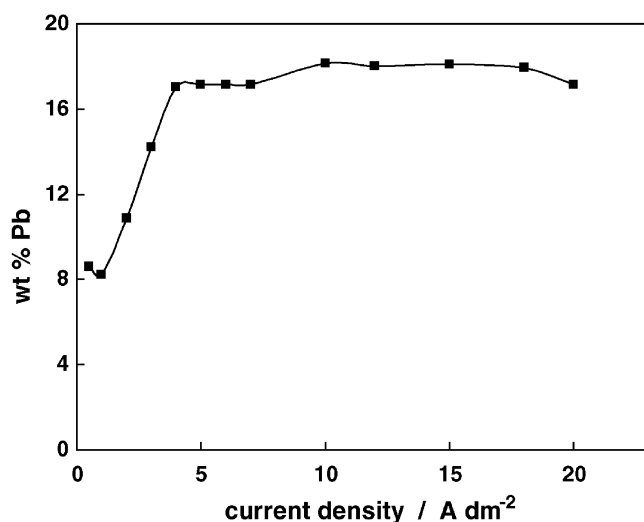

Fig. 1. Effect of current density on Sn–Pb deposit composition during DC plating onto a copper disk electrode at 500 rpm rotation speed from an electrolyte with composition given in Table 1.

3.2. *Effect of pulse frequency on deposit composition during PC and PR plating*

Typical examples of the input PC and PR current waveforms at low and high frequencies recorded on the digital oscilloscope are presented in Figure 2. Although not perfect square-wave waveforms, these signals closely fit the pre-set frequency, amplitude and duty cycle over each cycle. Figure 3 shows the effect of frequency on deposit composition during PC plating at an average overall current density of 3.78 A dm^{-2} and a duty cycle of 80%. The Pb content deposit varies only from 14 to 18 wt.% over the wide frequency range from 20 Hz to 200 kHz. These compositions are very close to the 17.1 wt.% Pb composition generated by DC plating at the same current density. Thus, on the basis of deposit composition alone, there does not appear to be an advantage to applying very high pulse frequencies. Although Kim et al. [13] investigated a much narrower frequency range than in the current study, they also observed pulse frequency to have little effect on alloy composition at an average current density of 10 A dm^{-2} at several duty cycles between 10 and 80%. Furthermore, this alloy content was very similar to that achieved by DC plating at the same current density.

Figure 3 also presents the effect of pulse frequency during PR plating from 20 Hz to 200 kHz with the cathodic pulse current density maintained at 6.3 A dm^{-2}, anodic pulse current density at 6.3 A dm^{-2} and the duty cycle at 80%. This corresponds to the same average current density of 3.78 A dm^{-2} applied during the PC plating experiments. Unlike that observed during PC electrolysis, frequency has a very large effect on deposit composition during PR plating. The Pb content varies widely depending on frequency, from a low value of 2.5% at 200 Hz to a high value of 28% at 20 kHz. These results are very interesting for a number of reasons. Firstly, it is possible to obtain deposits with a higher wt.% Pb than that of the plating bath. This is of potential practical benefit since it could allow Sn–Pb plating to be carried out from baths with much lower Pb contents than is currently possible. Also, the application of high frequency pulses yields deposits with Pb composition greater than the highest value possible (i.e., 18%) using DC plating.

Figure 4 shows the electrode potentials obtained during the PC and PR plating experiments shown in Figure 3 at 20 Hz and 20 kHz once a stationary state is reached. The response during cathodic polarization is very rapid so that the potential quickly reaches steady state between −0.65 and −0.70 V regardless of frequency and pulse mode. However, the response is slower once the current is turned off or reversed in polarity and does not reach steady state by the end of this portion of the pulse cycle. Thus, as frequency is increased, this portion of the electrode response is truncated, causing a negative shift in the electrode potential during both PC and PR plating. This appears to be a general phenomenon that was observed for a variety of pulse parameters.
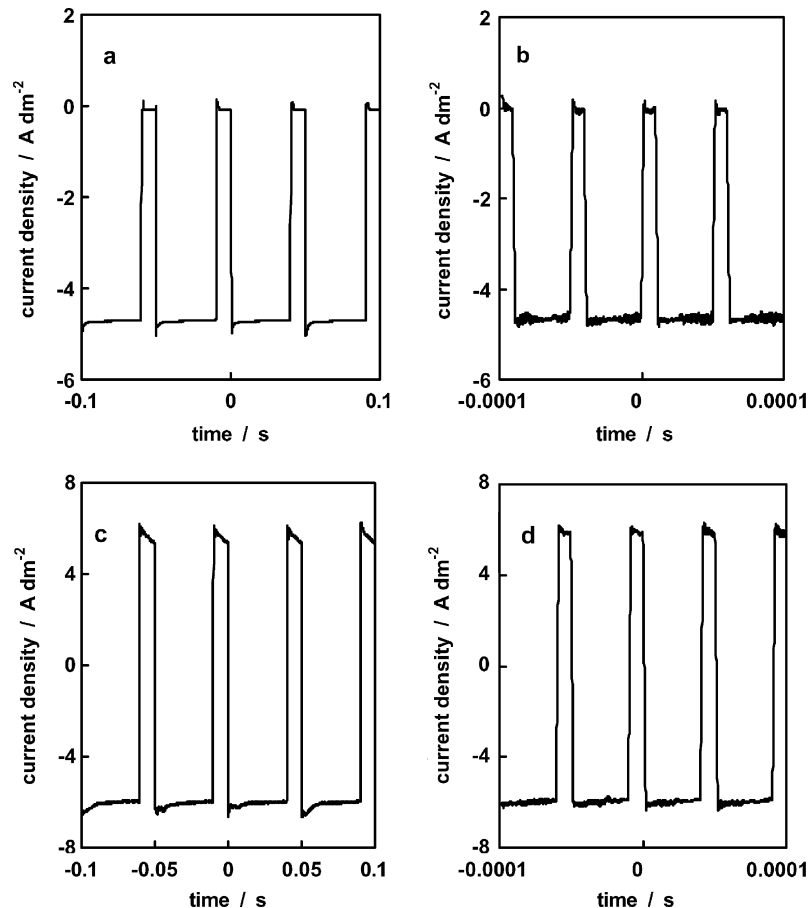
Fig. 2. Input current signal for 3.78 A dm^{-2} average current density at 80% duty cycle: (a) PC, 20 Hz (b) PC, 20 kHz (c) PR, 20 Hz (d) PR, 20 kHz.
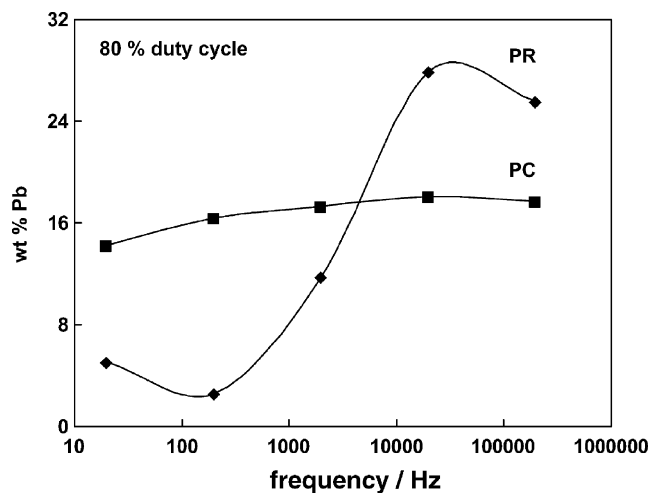

Fig. 3. Effect of frequency on Sn–Pb deposit composition during PC and PR plating at 3.78 A dm^{-2} average current density and 80% duty cycle.

The variation of alloy composition shown in Figure 3 mirrors the effect of frequency on the electrode potential reached by the end of the off-time during PC plating and the anodic pulse during PR plating. This observation suggests that differences in alloy composition may be traced primarily to events occurring during the off-time of the PC cycles or the anodic portion of the PR cycles.

In the case of PC plating, the effect of frequency is small, as reflected in the oscilloscope traces for 20 Hz and 20 kHz (Figure 4a and b) and those for the other frequencies studied. The electrode potentials reached during the off-time of PC plating at 20 Hz and 20 kHz are −0.37 and −0.48 V, respectively. A separate measurement has shown that the open-circuit potential of the alloy-coated electrode in the plating bath is −0.375 V. Thus, dissolution does not likely occur during the off-time at 20 kHz and, in fact, a small amount of deposition should continue to take place. This is possible because the changing electrode potential during the shift from the on-time to off-time generates an anodic capacitative current that must be offset by a cathodic faradaic current to yield an overall zero current. From the results of Petersson and Ahlberg [14, 15], Pb begins to deposit at a more positive potential than does Sn during alloy plating. Pb could then preferentially deposit during the off-time at high frequency pulse plating when the electrode potential is slightly below the open-circuit potential and a small cathodic faradaic current is flowing. This would cause the small increase in Pb content shown in Figure 3 as frequency increases during PC plating.

On the other hand, the large effect of frequency on alloy composition during PR plating is reflected in the electrode responses in Figure 4c and d showing elec-
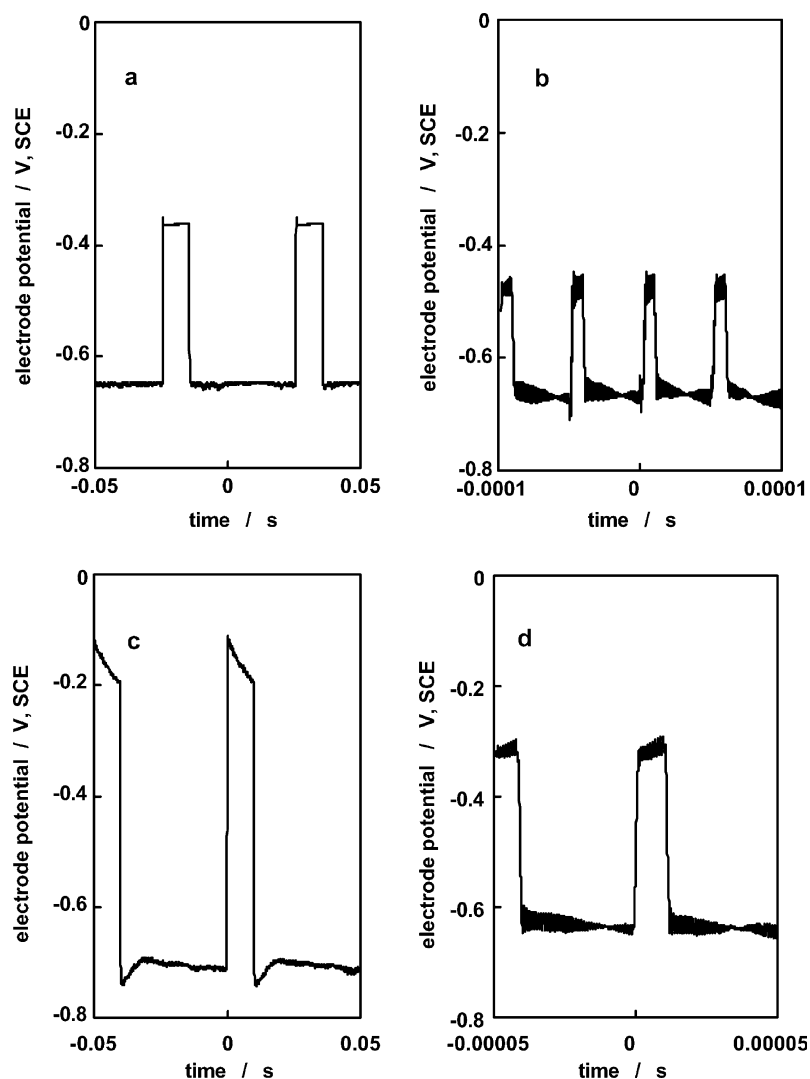
Fig. 4. Electrode response for 3.78 A dm^{-2} average current density, 80% duty cycle: (a) PC, 20 Hz, (b) PC, 20 kHz, (c) PR, 20 Hz and (d) PR, 20 kHz.

trode potentials of about −0.15 V at 20 Hz and −0.32 V at 20 kHz by the end of the anodic pulses. These potentials exceed the open-circuit value, indicating that dissolution of the deposited metals occurs during this part of the cycle. As shown previously [14, 15], Sn dissolves first as the electrode potential rises above the open-circuit potential. Consequently, at pulse frequencies of 20 and 200 kHz when the electrode potential only rises slightly above the open circuit value, Sn may preferentially dissolve and leave behind a deposit richer in Pb, as indicated in Figure 3. As the frequency decreases and a more positive electrode potential is reached during the anodic pulse, Pb more readily dissolves from the deposit, raising the Sn content.

Further analysis reveals that the final Pb content in the alloy is sensitive to the electrode potential reached during the anodic pulse. As shown in Figure 2c, a cathodic pulse amplitude of 6.3 A dm^{-2} is applied during the PR pulses at 80% duty cycle. From the DC results (Figure 1), this should yield an alloy containing slightly above 17 wt.% Pb by the end of the cathodic portion of the cycle. The results in Figure 3 indicate that an overall Pb content of 17 wt.% over an entire pulse cycle would require the use of a frequency of about 3 kHz. A lower frequency leads to a lower Pb content, whereas a higher frequency yields a higher Pb content. From the data in Figure 4c and d and at other frequencies (not included here), it appears that the alloy becomes richer in Pb than if produced by DC plating when the electrode potential remains below about −0.2 V during the anodic pulse. On the other hand, if the potential increases above −0.2 V, the opposite result occurs. Also, if the potential remains below about −0.2 V during the anodic pulse, the ratio of Pb to Sn dissolving is lower than the proportion in the alloy itself. Obviously, Pb dissolves out in a higher proportion if the potential rises above −0.2 V.

A second effect of frequency may involve the time available for metal dissolution during the anodic pulse. In the very short time available during PR plating at high frequency, Pb dissolution may not be able to keep
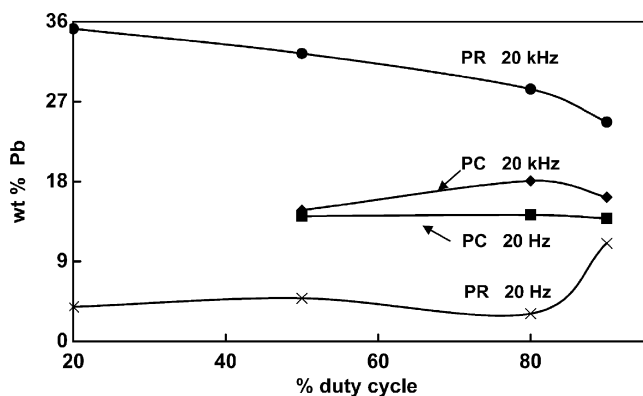
Fig. 5. Effect of duty cycle on Sn–Pb deposit composition during PC and PR plating at 3.78 A dm^{-2} average current density at 20 Hz and 20 kHz.

pace with Sn dissolution, leading to a higher overall Pb content in the resulting alloy.

Whether frequency affects deposit composition through electrode potential or the available time, a common factor may be the amount of metal dissolution occurring during the anodic pulses. When the extent of dissolution is small and limited to a small number of surface layers, Sn may be preferentially removed. However, when dissolution becomes more extensive, the surface region of the deposit would become depleted of Sn, thereby facilitating Pb dissolution.

The greater ability of the PR mode to alter deposit composition than the PC mode may stem from the fact that there is a larger separation in the electrode potentials at which the two metals dissolve than in the potentials at which they deposit [14, 15]. Thus, the overall alloy composition would be more sensitive to the potential reached during the anodic pulse of PR plating than to the potential reached during the off-time of PC plating.

3.3. *Effect of duty cycle on deposit composition during PC and PR plating*

The influence of duty cycle on deposit composition during PC plating for an average current density of

3.78 A dm^{-2} at 20 Hz and 20 kHz is presented in Figure 5. Three duty cycle values of 50, 80 and 90% were chosen in these experiments. The variation of duty cycle while maintaining the same average current density has little effect on composition during PC plating at any frequency. In order to maintain the same average current density, the magnitude of the current pulse during the on-time must increase as the duty cycle is reduced. This is reflected in the corresponding traces for duty cycles of 50 and 80% at 20 Hz and 20 kHz that show the electrode potential during the on-time becoming more negative with decreasing duty cycle (Figures 6 and 7). On the other hand, the potential reached during the off-time is only slightly more negative at 20 kHz than at 20 Hz for both duty cycles. The fact that Pb content in the alloy is not strongly affected by duty cycle at both frequencies provides additional evidence that deposit composition is more strongly affected by what occurs during the off-time than during the on-time.

The effect of duty cycle on Pb content during PR plating at 20 Hz and 20 kHz is also shown in Figure 5. The cathodic and anodic pulse amplitudes were adjusted to ensure that the same average current density of 3.78 A dm^{-2} was applied regardless of duty cycle and frequency. At 20 Hz, the Pb content in the deposit remains unchanged at about 4 wt.% for duty cycles between 20 and 80%. Further increase of the duty cycle to 90% leads to an increase in Pb content to 11%.

The electrode responses corresponding to the PR plating results at 20 Hz are presented in Figure 8. With increasing duty cycle, a positive shift in the electrode potential throughout the pulse cycle occurs, as expected. Despite significant differences in the electrode potentials during the cathodic pulses at 20 and 80% duty cycles, the resulting alloy compositions are very similar (Figure 5). It is likely that the Pb:Sn ratio deposited during the cathodic pulses is similar at the two duty cycles. This idea is supported by the observation that duty cycle has little effect on alloy composition during PC plating at any frequency. Furthermore, the alloy compositions produced by PC and DC plating are similar at the same
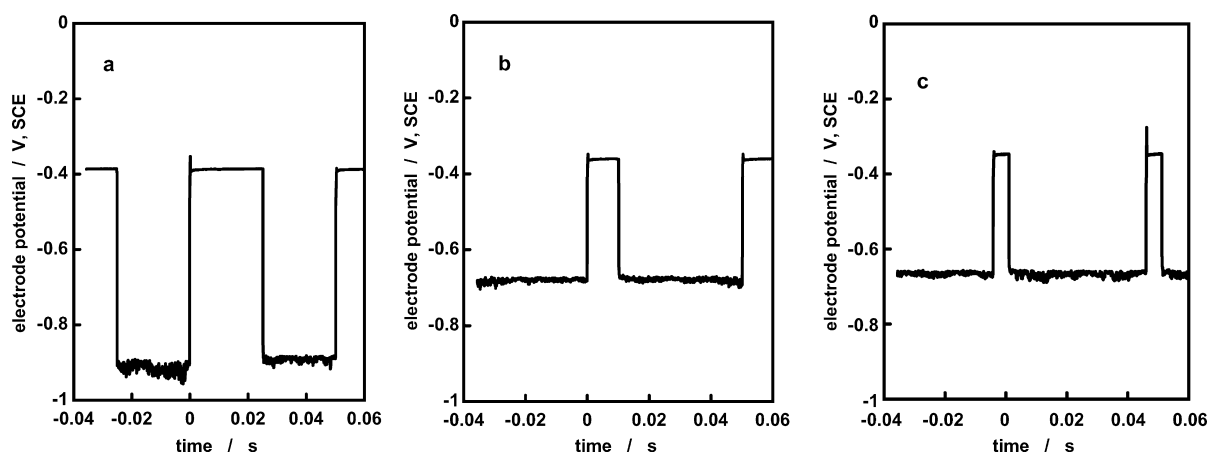

Fig. 6. Electrode response during PC plating at 20 Hz, 3.78 A dm^{-2} average current density and duty cycles (a) 50 (b) 80 and (c) 90%.
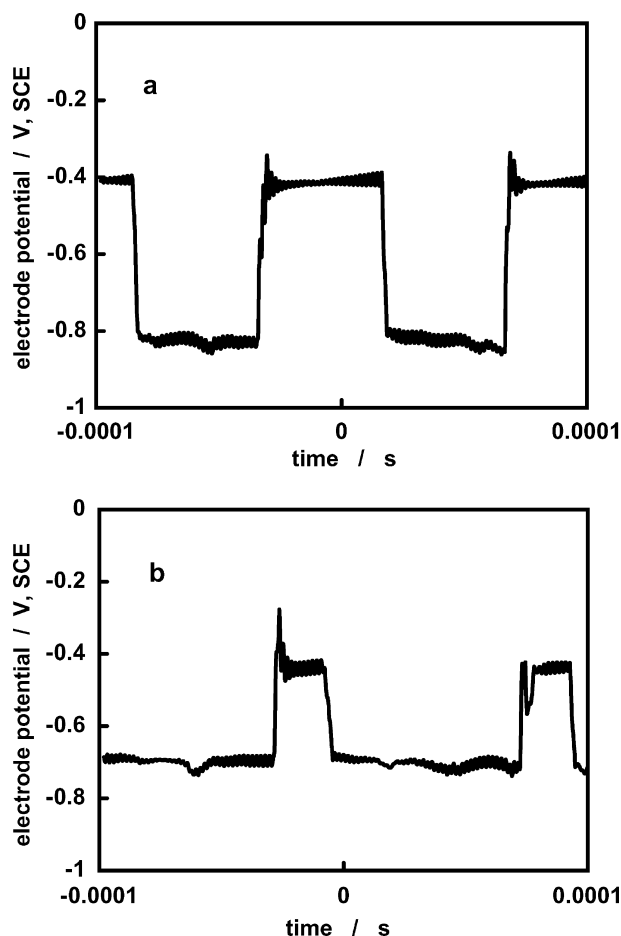
Fig. 7. Electrode response during PC plating at 20 kHz, 3.78 A dm^{-2} average current density and duty cycles (a) 50 and (b) 80%.
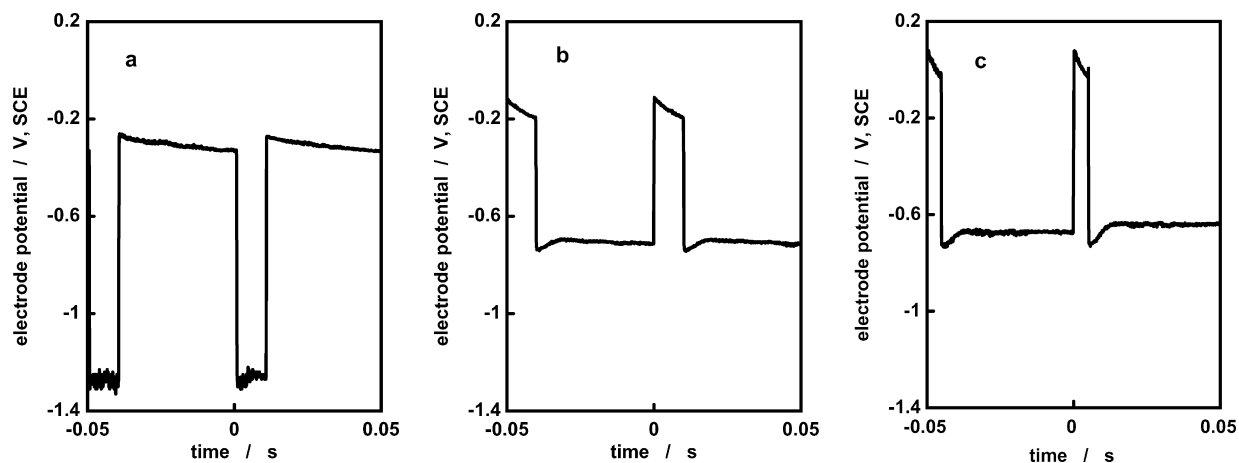

Fig. 8. Electrode response during PR plating at 20 Hz, 3.78 A dm^{-2} average current density and duty cycles (a) 20 (b) 80 and (c) 90%.

average current density. The DC plating results also indicate that current density does not affect deposit composition once it exceeds about 4 A dm^{-2} (Figure 1). If the system reaches steady state by the end of the cathodic pulse at 20 Hz, then the additional current density applied during the cathodic pulse at 20% duty cycle over that at 80% duty cycle would not significantly alter the deposit composition from 17–18 wt.% Pb. Since the resulting Pb content over the entire pulse cycle

is only about 4 wt.% at 20% duty cycle (Figure 5), it appears that Pb preferentially dissolves during the anodic pulse, as at 80% duty cycle. The rise in Pb content to 11 wt.% at 90% duty cycle is likely due to the relative proportion of cathodic and anodic pulse times. A pulse with 90% duty cycle approaches a DC input signal and the time available for metal dissolution becomes limited. Thus, a change from 80 to 90% would be expected to shift the deposit composition toward

the 17 wt.% Pb level obtained during DC plating (Figure 1).

The behaviour of the system at a PR frequency of 20 kHz, on the other hand, differs significantly (Figure 5). An increase of duty cycle from 20 to 90% causes the Pb content in the deposit to decrease from 35 to 24%. A comparison of the two curves in Figure 5 highlights the strong effect that pulse frequency has on the behaviour of the Sn–Pb system. Consistent with the previous section is the observation that a higher Pb content is achieved at 20 kHz for all duty cycles. The most striking example occurs at 20% duty cycle where a 4 wt.% Pb content is produced at low frequency, but 35 wt.% at high frequency. This Pb content of 35% is the highest level achieved in this study.

The previous explanation of the effect of frequency on composition is also consistent with the effect of duty cycle at 20 kHz (Figure 5). To maintain a constant average current density and the charge passed during the cathodic and anodic pulses, the magnitude of the anodic pulse increases as the duty cycle is raised, causing a positive shift in electrode potential (Figure 9). As discussed previously, a higher potential during the anodic pulse should lead to a lower Pb content in the deposits. As expected, the increase in duty cycle from 80 to 90% causes the input current to approach that of DC

electrolysis and the resulting Pb content to decrease toward the value obtained via DC plating.

However, the potential reached during the anodic pulse cannot explain all the observed effects. As mentioned previously, the difference in Pb content in the deposits produced at 20 Hz and 20 kHz is greatest at a 20% duty cycle. This is the very condition where the difference in electrode potentials during the anodic pulse is the smallest. A second hypothesis offered previously was that shortening the anodic pulse causes a higher Pb content due to faster Sn dissolution. However, since the anodic pulse becomes shorter as duty cycle rises, this explanation is inconsistent with the observed decline in Pb content (Figure 5). Thus, neither of these explanations alone can explain all of the observed trends and perhaps some combination of these factors is operative.

3.4. *Effect of cathodic pulse amplitude on deposit composition during PR plating*

Since PC pulse parameters have been found to not strongly influence deposit composition, the effect of cathodic pulse amplitude was investigated only for PR mode. An increase in the cathodic pulse amplitude while maintaining the other pulse parameters fixed should
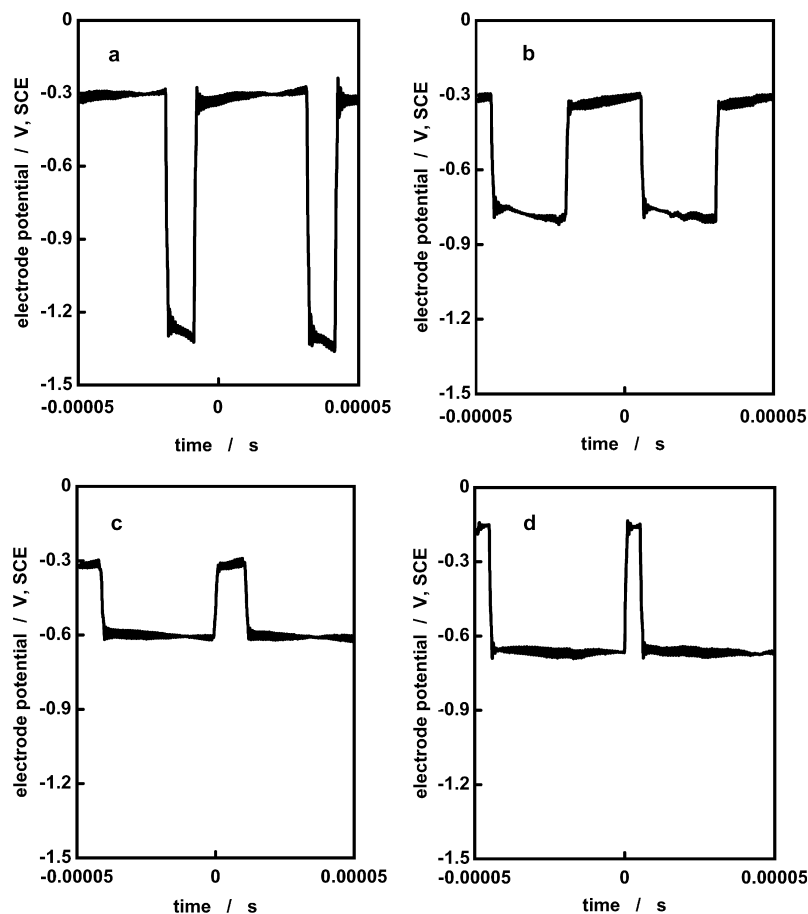

Fig. 9. Electrode response during PR plating at 20 kHz, 3.78 A dm^{-2} average current density and duty cycles (a) 20 (b) 50 (c) 80 and (d) 90%.
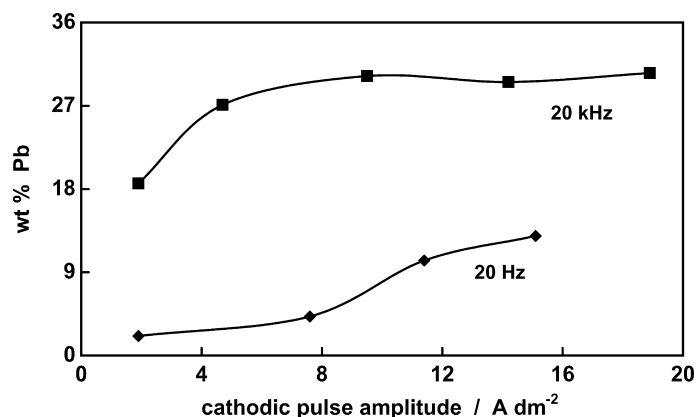
Fig. 10. Effect of cathodic pulse amplitude on Sn–Pb deposit composition during PR plating at 20 Hz and 20 kHz, 80% duty cycle and 4.7 A dm^{-2} anodic pulse amplitude.

have the same effect as increasing the applied current during DC plating. Thus, it is not surprising that the Pb content increases with cathodic pulse amplitude at 20 Hz for 80% duty cycle (Figure 10). The cathodic pulse amplitude was varied from 1.9 to 15.0 A dm^{-2} at 20 Hz, while the anodic pulse amplitude was maintained at 4.7 A dm^{-2}. This corresponds to overall cathodic current densities from 0.6 to 11.1 A dm^{-2}. The corresponding wt.% Pb increases from slightly above 4% to about 16%. When the cathodic pulse amplitude is raised to 18.9 A dm^{-2}, the deposit surface becomes very rough, suggesting that mass transport is becoming important.

The corresponding electrode potential traces for the 20 Hz pulses are given in Figure 11. Predictably, the electrode potential during the cathodic pulses shifts negatively as the cathodic pulse amplitude rises. On the other hand, the potential reached during the anodic pulse remains essentially constant. The electrode response during the anodic pulse can keep up with the rate
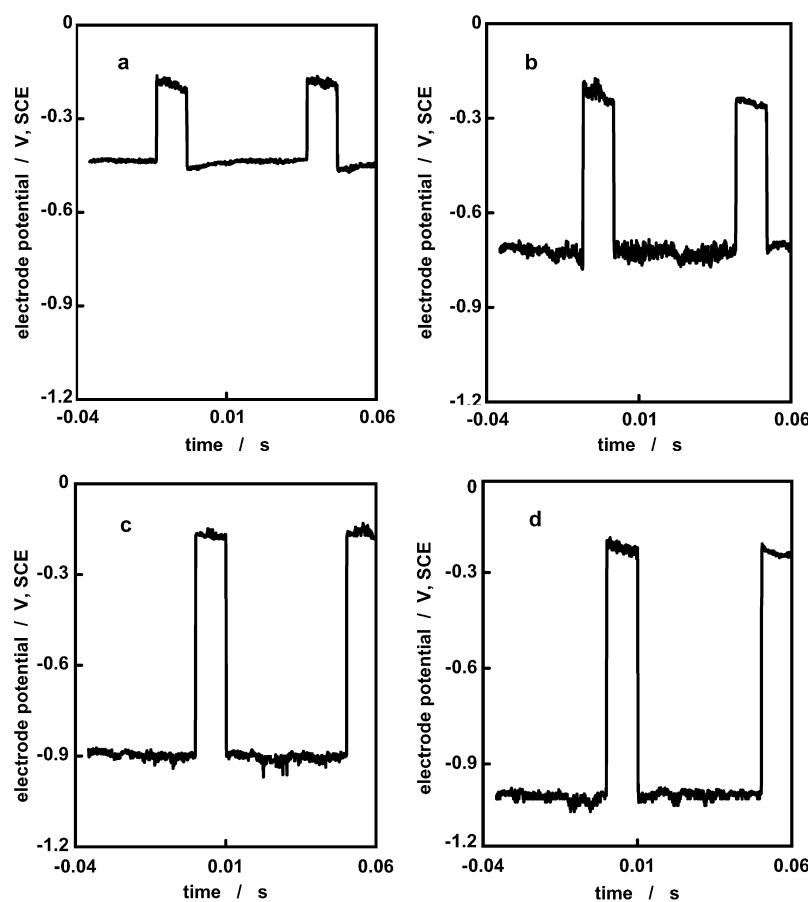

Fig. 11. Electrode response during PR plating at 20 Hz, 80% duty cycle, 4.7 A dm^{-2} anodic pulse amplitude and cathodic pulse amplitudes (a) 1.9 (b) 7.6 (c) 11.4 and (d) 15.1 A dm^{-2}.

of change of the applied current at this low frequency. It is noteworthy that the electrode potentials reach about −0.2 V during the anodic pulse in all cases in Figure 11 and the corresponding Pb content is always less than that obtained by DC plating at the same current. A similar trend was observed in Section 3.2.

The effects of cathodic pulse amplitude on Pb content and electrode potential response at 20 kHz are presented in Figures 10 and 12. The Pb content rises with increasing cathodic pulse amplitude as at 20 Hz, but as observed previously, it is always higher at the high frequency. Moreover, the Pb content levels off at about 29–30 wt.% when the cathodic pulse amplitude exceeds 9.4 A dm^{-2} or so.

The traces in Figure 12 show the expected negative shift in electrode potential during the cathodic pulse similar to that observed for the lower frequency (Figure 11). However, an appreciable negative shift in the potential during the anodic pulse is also evident. This is not seen at 20 Hz and suggests that the electrode response cannot keep up with the rate of change of the applied current at 20 kHz. The more negative the potential during the cathodic pulse, the less the potential rises during the anodic pulse. The potential always remains below −0.2 V and the corresponding Pb content exceeds

that obtained during DC plating at the same current. The electrode potentials during the anodic pulses after low amplitude cathodic pulses reach just above the open-circuit potential, while those after high amplitude cathodic pulses never attain this potential. Thus, in the latter case, metal dissolution will not occur and a small amount of deposition can continue during the anodic pulse, similar to what takes place during PC plating.

Examination of the deposits obtained at 20 kHz shows that very rough surfaces characteristic of mass transport control conditions are not produced until the cathodic pulse amplitude reaches 30 A dm^{-2}, much higher than the level at 20 Hz. This agrees with the boundary layer model for pulse plating which predicts a frequency increase to make the inner diffusion layer thinner and raise the limiting cathodic pulse current [20].

4. Conclusions

The effects of PC and PR modes on the composition of Sn–Pb coatings deposited on a copper rotating disk from fluoroborate solutions have been investigated over a wide range of pulse frequencies (20 Hz–200 kHz), duty cycles and cathodic pulse amplitudes. Under DC
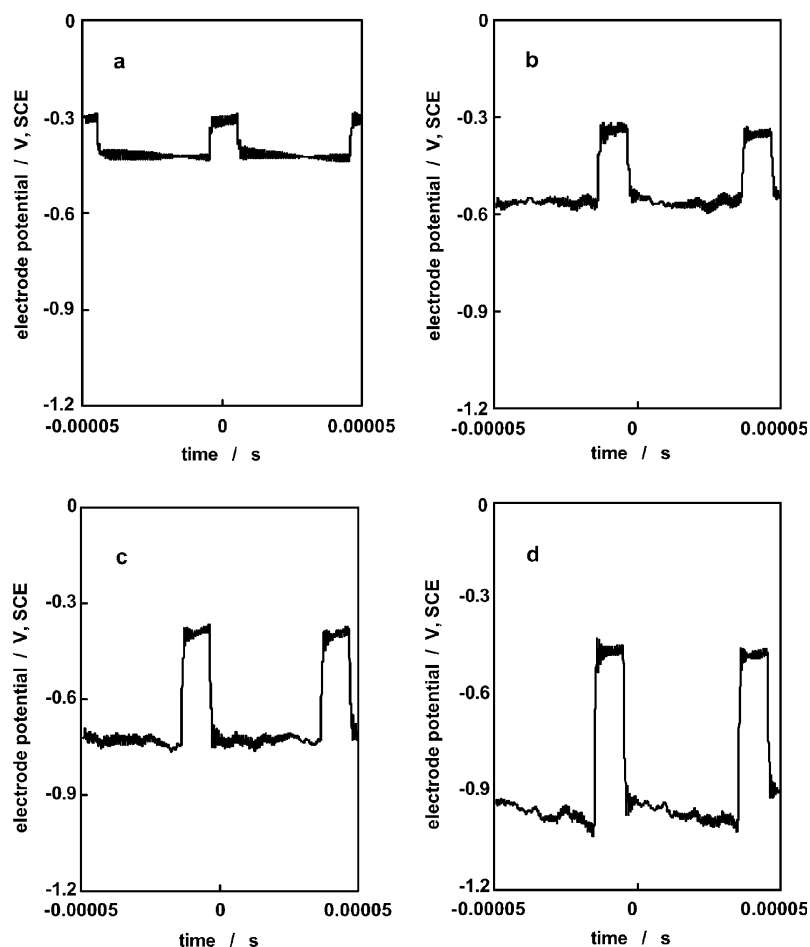

Fig. 12. Electrode response during PR plating at 20 kHz, 80% duty cycle, 4.7 A dm^{-2} anodic pulse amplitude and cathodic pulse amplitudes (a) 1.9 (b) 4.7 (c) 9.5 and (d) 14.2 A dm^{-2}.

conditions, the Pb content in the alloys rises from 8.2 wt.% to slightly above 18 wt.% as the current density is increased from 0.5 to 20 A dm^{-2}. The effects of pulse parameters on alloy composition differ dramatically depending on the mode of electrolysis being used. Composition is only mildly influenced by frequency and duty cycle during PC plating and does not vary significantly from that obtained by DC plating. On the other hand, use of the PR mode dramatically alters composition depending on pulse frequency, duty cycle and amplitude, yielding alloys with Pb content both well above and below that achievable by DC plating. The Pb content varies from 2.5 to 28 wt.% over the frequency range from 20 Hz to 200 kHz using the same plating bath, with duty cycle and average current density fixed at 80% and 3.78 A dm^{-2}. At a 20 Hz frequency, the proportion of Pb in the resulting alloy is always lower than that in the solution regardless of the other parameters. On the other hand, the proportion of Pb in the alloy almost always exceeds that in the solution when a 20 kHz frequency is imposed.

Monitoring of the electrode potentials suggests that the alloy composition is most critically affected by events occurring during the off-time of PC plating or anodic pulses of PR plating. The large range of compositions obtained by PR plating may be due to changes in the relative rates of Sn and Pb dissolution during the anodic pulse depending on the electrode potential reached during the anodic pulse and/or the duration of the anodic pulse. Less positive electrode potentials and shorter anodic pulse times, which are favoured at high frequencies, tend to yield alloys with higher Pb content. A similar explanation applies to PC plating, although the variations in composition are small.

Finally, the results of this study may be important for the recent efforts to reduce or completely eliminate the amount of Pb in Sn–Pb alloys due to environmental concerns. The use of high frequency PR plating may allow a desired alloy composition to be obtained from a plating bath with a lower Pb content than is otherwise possible.

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