

Pulse Plating of Silver-Palladium Alloys

By Dong Shou-Jiang, Y. Fukumoto and T. Hayashi

Current pulses at 200 to 400 mA/cm² with an on-time of 0.1 msec and an average current density of 4 mA/cm² were the optimum pulsing conditions for depositing bright, smooth silver alloy containing about 25 percent palladium. Deposit composition appeared to be controlled by diffusion polarization. A high overpotential during pulse plating seemed effective for the formation of fine-grained alloy deposits.

Silver-palladium alloys have found many applications in the electronic industry as a replacement for hard gold on electrical contacts.¹ Although thiocyanate,² cyanide³ and chloride⁴ baths have been studied, no practical process for plating Ag-Pd alloys from these solutions has been developed, because the deposits had a poor appearance and were limited to a narrow range of alloy composition.

Dossenbach, Sturzenegger and Puipe⁵ recently examined with promising results the deposition of Ag-Pd alloy in an ammoniacal nitrate bath and studied changes in surface features, composition and deposit properties as a function of pulse plating parameters. However, the silver and palladium were deposited at significantly different potentials, so alloy composition was hard to control.

We recognized in a preliminary study that both silver and palladium can be deposited at nearly the same potential in a complexed bromide bath and studied the possibility of controlling surface structure and composition by using pulse plating with this solution.

The structure of electrodeposits is strongly affected by the high cathode potentials encountered in pulse plating. In alloy deposition, the ion concentration at the electrode surface also will influence results. Changes in the concentration of depositable ions in the vicinity of the cathode surface is less influential during pulse plating than during direct-current plating, however.

In our study of Ag-Pd alloy plating, rectangular current pulses were applied at different pulse current densities, duty cycles and average current densities and an attempt was made to deposit smooth and fine-grained deposits. Changes in the composition and structure were studied as a function of both total current per pulse and average current density while decisive factors affecting composition and structure were explored.

Experimental Procedure

Platinum-clad tantalum was the anode, and polycrystalline copper with an area of about 1 cm² was the cathode. The copper coupons were electropolished and electroplated with about 10 μm of silver at a current of 8 coulombs prior to Ag-Pd alloy deposition. The electrolyte used in this study was composed of 0.1 M K₂(PdBr₄), 0.05 M AgBr, 6.5 M NaBr and 2.5 mM Ce(SO₄)₂, adjusted to a pH of 4 to 4.5 with

NaOH. In the unstirred bath at 45° C, alloy coatings of 3-μm-thick were deposited at 6 coulombs to prepare samples for inspecting surface morphology and determining alloy composition. The electrode potential was measured with an oscillograph just before the current was switched off.

Table 1 shows the current wave forms used in this study. Experiments with constant average current density were conducted with variable pulse current density (*i_p*) and variable on- and off-times (*t_{on}* and *t_{off}*). Changes in the concentrations of metal ions in the cathode diffusion layer were rather small with the pulsed cycles we adopted, permitting an evaluation of the influence of the electrode potential on alloy deposition. To determine the influence of the concentration of metal ions, experiments with variable average current density were also conducted using variable pulse current density and off-time.

The morphology of the alloy deposits was examined by scanning electron microscopy (SEM). X-ray diffraction analysis with CuKα radiation was used to estimate alloy composition and preferred orientation. Because Ag-Pd alloys form solid solutions, the alloy composition could be estimated by determining the lattice constants of the alloy deposits from X-ray diffraction data.⁶ The amount of hydrogen absorbed in the deposits was estimated by measuring the current consumed for the anodic oxidation of hydrogen by a procedure conducted at 0.2 V vs. Hg/HgO in an alkaline solution within 10 sec after electrodepositing the alloy.⁷

Alloy Composition

Figure 1 shows steady-state polarization curves for the deposition of silver, palladium and Ag-Pd alloy from their bromide baths. Because palladium is deposited in preference to silver and the limiting rate for palladium deposition is smaller than that for silver, the limiting current density for palladium deposition is a decisive factor. The limiting current density obtained from the steady-state polarization curve was 4.5 mA/cm² when the electrolyte contained 0.1 M K₂(PdBr₄) and 6.5 M NaBr.

Assuming that the thickness of the diffusion layer (*δ*) adjacent to the cathode surface is 0.05 cm, the diffusion coefficient (*D*) of palladium in this electrolyte is estimated as 10⁻⁶ cm²/sec. The limiting pulse current density for our experimental conditions can be calculated by inserting these values into Ibl's equation?

$$i_p(\text{lim.}) = i_{\text{lim}} \{ [2Dt_{\text{on}}(1-X)/\delta^2]^{0.5} [X^{-1}-1] + 1 \}^{-1} X^{-1}$$

where the duty cycle $X = t_{\text{on}}/(t_{\text{on}} + t_{\text{off}})$. The limiting pulse current densities calculated for different duty cycles are given in Table 1.

With direct or pulsed-current plating at an average current density above 5 mA/cm² and pulsed plating with a pulse current density above 40, 200 and 300 mA/cm²

Table 1
Waveforms, Limiting Pulse Current Densities
and Appearance of Ag-Pd Alloy Deposits

On-time, msec	Off-time, msec	Duty Cycle	Pulse current density, mA/cm ²	Limiting current density, mA/cm ²	Average current density, mA/cm ²	Appearance
0.1	0.4	0.2	20	23	4	Semibright
0.1	0.9	0.1	40	45	4	Semibright
0.1	4.9	0.02	200	222	4	Bright
0.1	9.9	0.01	400	438	4	Bright
1	4	0.2	20	23	4	
1	9	0.1	40	45	4	
1	49	0.02	200	215	4	
1	99	0.01	400	410	4	Dull
10	490	0.02	200	198	4	
10	990	0.01	400	350	4	Dull
1	9	0.1	20	45	2	
1	49	0.02	20	215	0.4	
1	4	0.2	40	23	8	Black
1	5	0.17	40	27	6.7	Dull
1	10	0.09	40	49	3.6	Dull
1	20	0.048	40	93	1.9	Dull
1	39	0.025	200	174	5	
1	399	0.0025	200	1370	0.5	
0.1	4.9	0.02	100	222	2	Dull
0.1	4.9	0.02	300	222	6	Semibright
0.1	4.9	0.02	400	222	8	Dull
Direct current				4.5	2	Dull
Direct current				4.5	3	Semibright
Direct current				4.5	4	Semibright
Direct current				4.5	5	Dull
Direct current				4.5	6	Black

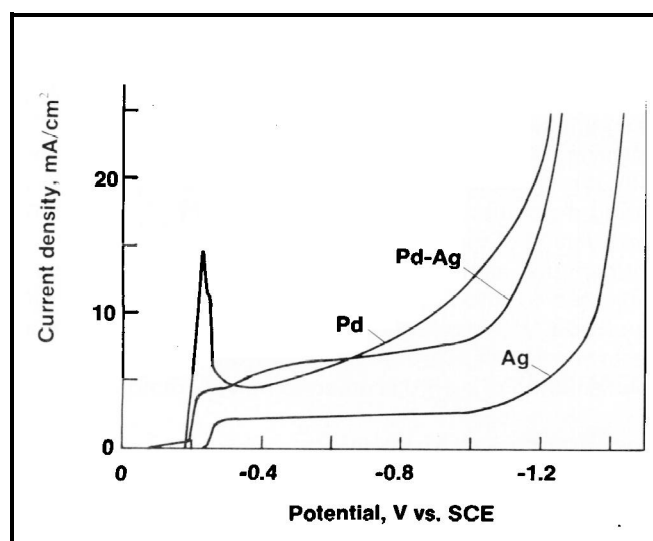


Fig. 1—Cathodic polarization data.

combined with a $t_{on}(msec)/t_{off}(msec)$ ratio of 1:4, 1:39 and 0.1:4.9, respectively, the pulse current density approached the theoretical limiting current density, resulting in depletion of palladium ions in the vicinity of the cathode surface. Under these conditions, the concentration polarization would be expected to have a significant influence on the composition and properties of the Ag-Pd alloy deposits.

When the pulse current density, on-time or average current was decreased, the pulse current density was lower than the limiting current density of the pulse. In such cases, the influence of changes in ion concentrations at the cathode surface appeared to be negligible.

The effects of changing the pulse current density and on-time on the electrode potential and on the composition of the deposits during Ag-Pd pulse plating at a constant average current density are shown in Figs. 2 and 3. The electrode potential for alloy deposition shifted to the less noble direction with an increase in the pulse current density or on time. Based on thermodynamic data, an increase in the rate of silver deposition was expected in preference to

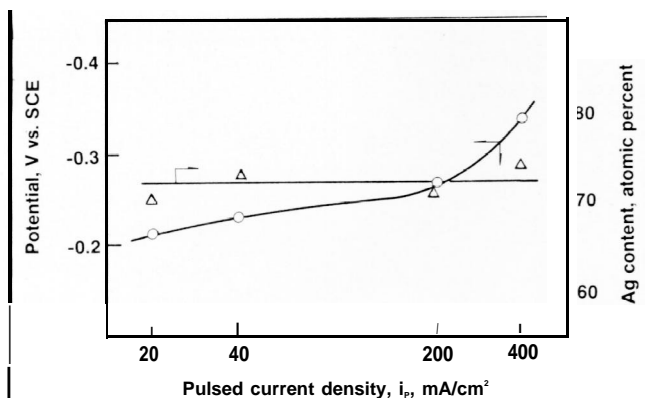


Fig. 2—Effect of pulse current density (i_p) on the cathode potential and the silver content of the deposits. O = t_{on} 1 msec, i_m 4 mA/cm²; Δ = t_{on} 0.1 msec, i_m 4 mA/cm².

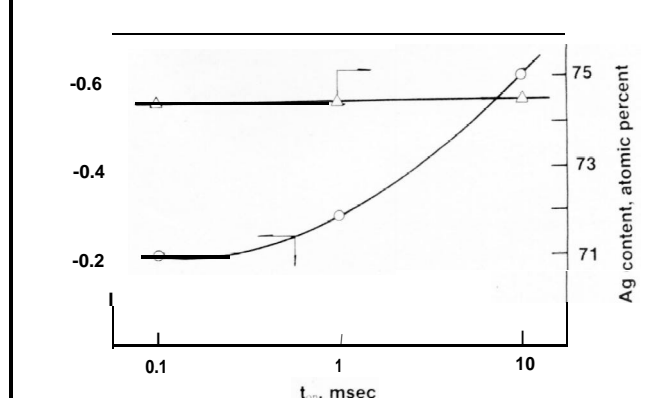


Fig. 3—Effect of on-time on the cathode potential and the silver content of the deposits. O = i_p 200 mA/cm², i_m 4 mA/cm²; Δ = i_p 400 mA/cm², i_m 4 mA/cm².

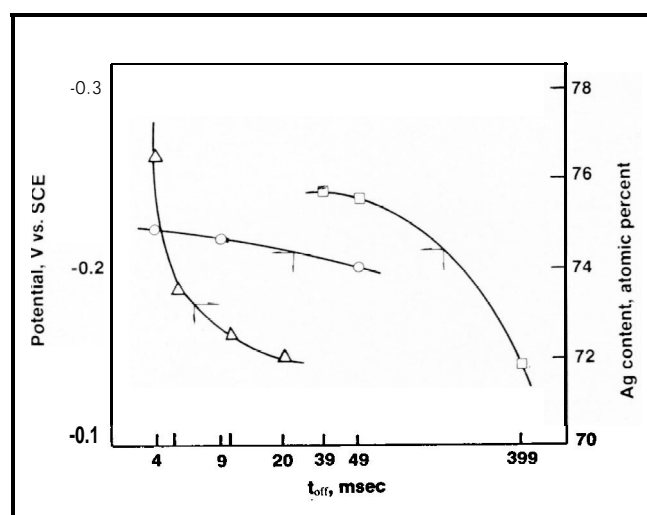


Fig. 4—Effect of off-time on the cathode potential and the silver content of the deposits. O = t_{on} 1 msec, i_p 20 mA/cm²; \square = t_{on} 1 msec, i_p 200 mA/cm²; Δ = t_{on} 1 msec, i_p 40 mA/cm².

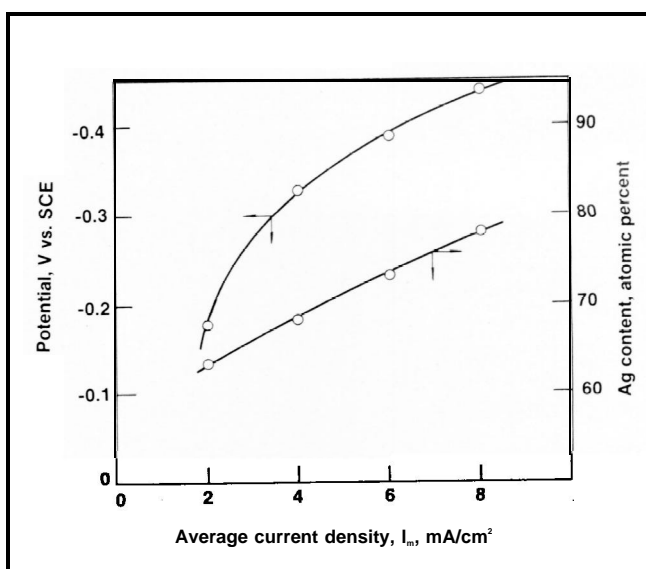


Fig. 5—Effect of average current density (i_m) on the cathode potential and silver content of pulse-plated deposits, with on-time of 0.1 msec and off-time of 4.9 msec.

the palladium deposition rate when the pulse current density or on-time was increased. However our data (Figs. 2 and 3) show that the composition of the alloy was essentially unaltered with increasing pulse current density or on-time. With a constant average current density, an increase in the pulse current density or an increase in on-time accompanied an increase in the off-time. Because the palladium ion concentration at the cathode surface was restored during long off-time periods, an increase in the palladium content of the deposit was expected with the longer off-times. The effect of the increase in off-time evidently balanced the expected influence of the electrode potential data. Thus, the deposit composition depends not only on electrode potentials but also in the concentration of depositable ions in the diffusion layer.

With increasing off-time, the electrode potential shifted towards the noble direction, as shown in Fig. 4. The expected influence of increasing off-time was confirmed by the decrease in the silver content of the deposits.

Figures 5 and 6 show the changes in the electrode potential and the silver content of the deposits during deposition with pulsed and direct current, respectively, as a function of the average current density. The negative shift in potential with increasing average current density. The

silver content of the alloys increased with an increase in the average current density, but the trend was more significant with direct-current plating than with pulsed-current plating.

Polarization was greater during pulse plating than during direct-current plating. The content of the less noble silver was expected to be higher in the pulse-plated deposits. However, our results showed much higher silver contents with direct current, which indicates that the potential during deposition is not the decisive factor governing the composition of the Ag-Pd alloy deposits.

When the deposits obtained during this study were subjected to anodic oxidation at 0.2 V vs. the Hg/HgO electrode, no evidence of hydrogen oxidation was observed. The resorption rate of hydrogen absorbed in the solid solution of Ag-Pd seemed to be very rapid.

Appearance and Morphology

Bright and smooth Ag-Pd deposits were obtained when the current was pulsed at a high current density of 200 or 400 mA/cm², an average current density of 4 mA/cm² and an on-time of 0.1 msec. These were the best conditions for the

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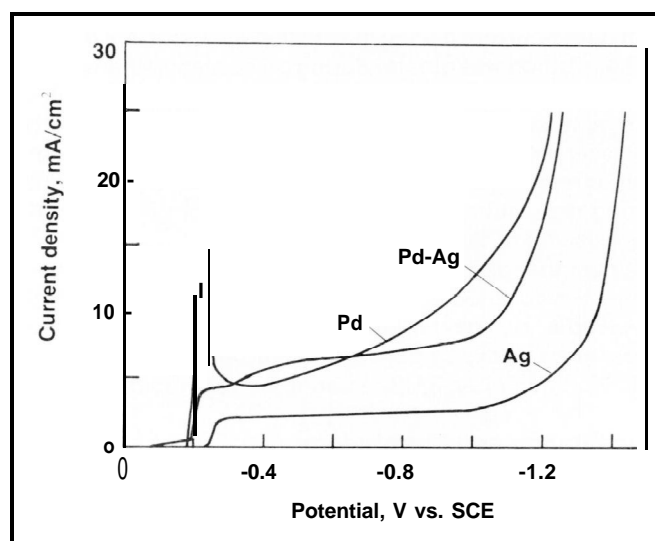


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combined with a $t_{on}(msec)/t_{off}(msec)$ ratio of 1:4, 1:39 and 0.1:4.9, respectively, the pulse current density approached the theoretical limiting current density, resulting in depletion of palladium ions in the vicinity of the cathode surface. Under these conditions, the concentration polarization would be expected to have a significant influence on the composition and properties of the Ag-Pd alloy deposits.

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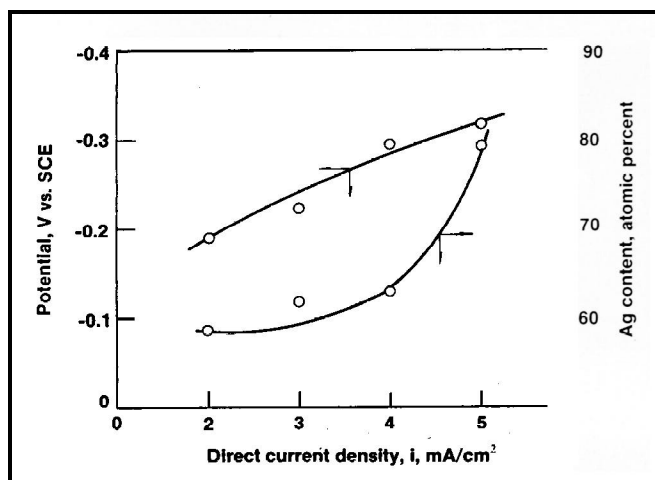


Fig. 8—Effect of direct current density on the cathode potential and silver content of the deposits.

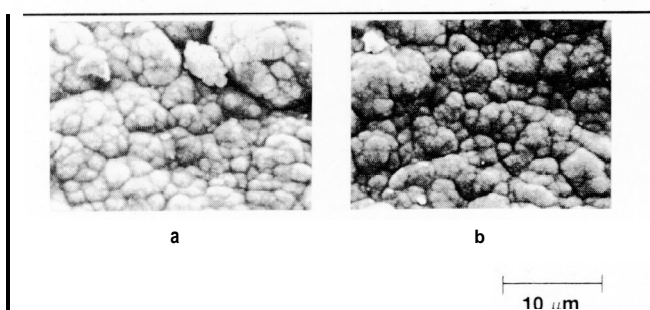


Fig. 8—SEM photographs showing surface views of Ag-Pd deposits obtained at an average current density of 4 mA/cm², a pulse current density of 400 mA/cm². On-time was (a) 0.1 and (b) 10 msec.

formation of good alloy deposits. With longer on-time periods of 1 or 10 msec, deposits were dull, as shown in Table 1. Alloys deposited with pulsed current, an on-time of 0.1 msec and an average current density of 6 mA/cm² had the same semibright appearance as direct-current deposits obtained at 3 or 4 mA/cm². The direct- and pulsed-current alloys deposited at 2 mA/cm² were dull, however.

Typical SEM photographs of Ag-Pd alloy deposits produced with pulsed current are shown in Figs. 7 and 8 as a function of the pulse current density and on-time, respectively. The deposits obtained in this study had a rather coarse, nodular morphology. The mean diameter of

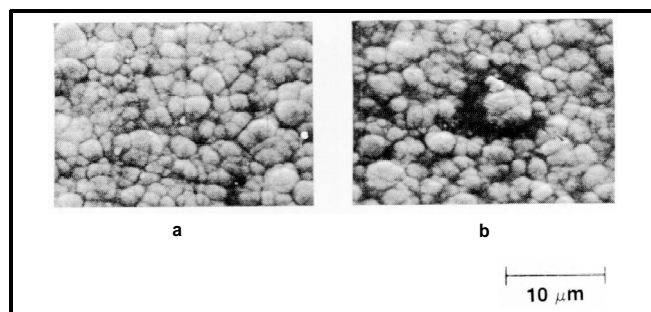


Fig. 7—SEM photographs showing surface views of Ag-Pd deposits obtained with an average current density of 4 mA/cm² and an on-time of 0.1 msec. Pulse current density was (a) 20 and (b) 200 mA/cm².

the nodules was in the range of 1 to 5 μm. The difference in the size of the nodules with changes in the pulse current density or on-time is not considered significant.

Figures 9 and 10 show the influence of changing the off-time and average current density, respectively, on the morphology of the alloy deposits. The deposits obtained with 2 mA/cm² of direct current had fairly flat nodules. Increasing the dc to 4 mA/cm² resulted in rounded nodules with coarse subgrains. The nodules on deposits obtained with pulsed current were smaller than those on direct-current deposits.

Table 2 shows the grain size estimated from the half-width of the (111) peak in the X-ray diffraction profiles of the Ag-Pd deposits. An increase in the pulse current density, the average current density or the on-time refined the grain size. These trends agreed with the electrode potential data obtained during deposition and can be interpreted as an acceleration in the nucleation rate. An increase in the overpotential and concentration of the adatom produced more nuclei which resulted in finer-grained alloy deposits.

The structural features in the electrodeposited Ag-Pd alloys seemed to be in accord with changes in the electrode potential of the working electrode. Thus the electrode potential appears to be the dominant factor affecting structure—in the same way observed previously during a study of the electrodeposition of unalloyed palladium.

All Ag-Pd alloy deposits produced during this study showed a preferred orientation of the (111) plane. Pulse plating conditions appeared to have no influence on the orientation index.

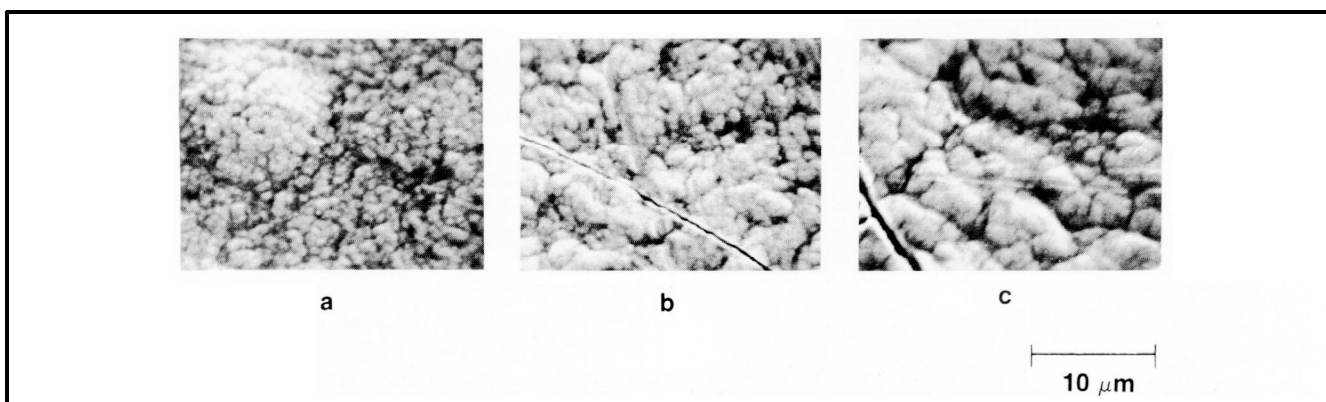


Fig. 9—SEM photograph showing surface views of Ag-Pd alloy deposits obtained with a Pulse current density of 40 mA/cm² and an on-time of 1 msec. Off-time was (a) 4, (b) 10 and (c) 20 msec.

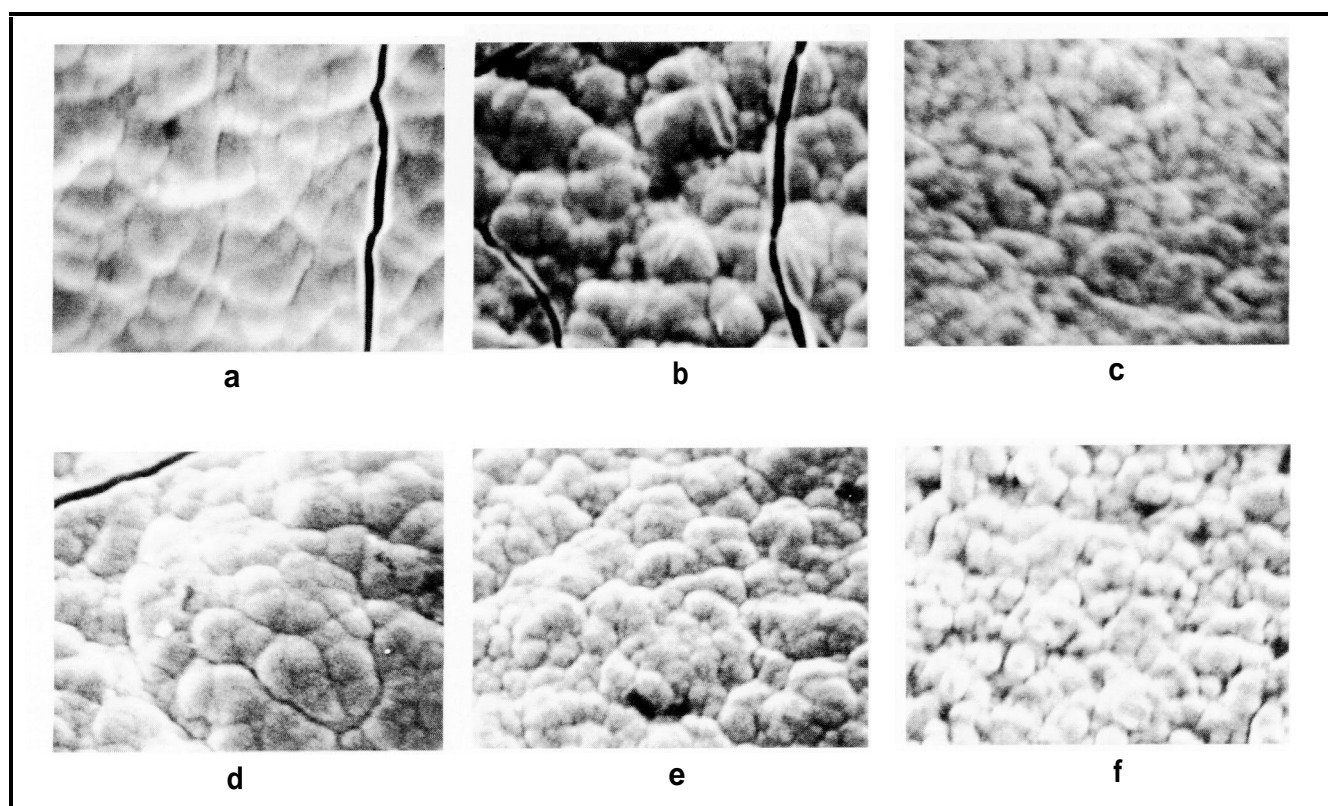


Fig. 10—SEM photographs of Ag-Pd alloys plated with direct-current at (a) 2, (b) 3, and (c) 5 mA/cm² or with pulsed current with an on-time of 0.1 meet and off-time of 4.9 msec at average current density of (d) 2, (e) 4 and (f) 6 mA/cm².

10 µm

Table 2
Grain Size of Ag-Pd Alloy Deposits

On time, msec	off time, msec	Average current density, mA/cm ²	Grain size, µm
0.1	0.4	4	200
0.1	0.9	4	85
0.1	9.9	4	70
1	99	4	55
10	990	4	35
1	4	8	50
1	5	6.7	60
1	10	3.6	70
1	20	1.9	120
0.1	4.9	2	175
0.1	4.9	4	145
0.1	4.9	6	70
0.1	4.9	8	65
Direct current		2	225
Direct current		3	175
Direct current		4	145
Direct current		5	75

Conclusions

The deposition of silver and palladium occurs at about the same potential in the bromide bath used during this study. The silver content of the Ag-Pd alloys increased with an increase in the average current density, but this trend was less pronounced with pulsed-current plating than with direct-current plating. An increase in the off-time reduced the silver content. The chief factor affecting the alloy composition seems to be the concentration of depositable ions in the vicinity of the cathode surface.

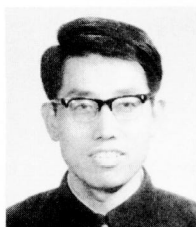
An increase in the average current density, the pulse current density or the on-time during electrodeposition led to a high overpotential and produced fine-grained deposits. The formation of smooth and bright alloy deposits during pulsed-current plating seems to be attributable to a high overpotential. Structural features such as surface morphology and grain size seems to depend on the amount of energy supplied for the crystallization process of metals.

The optimum pulsing conditions for obtaining smooth, bright silver-palladium alloy deposits are a pulse current density of 200-400 mA/cm², an average current density of 4 mA/cm² and an on-time of 0.1 msec.

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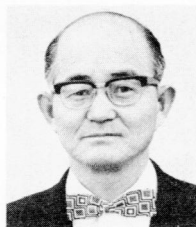
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