Pulsed Current Electroplating Of Silver-Gallium Alloy

By W. Reksc, K. Jurewicz and E. Frackowiak

The codeposition of 4.0 to 4.5 percent gallium increases the hardness of silver and improves wear resistance fourfold with only an insignificant increase in electrical resistivity. Electrodeposits containing up to 15 percent gallium were obtained with short rectangular pulses between longer off-time periods. Pulse duration and current density proved to be important factors for depositing coherent, dense alloy. A 0.10 to 0.18 sec pulse, a pulse current density of 16 to 20 A/dm^2 and an off-time of 13 to 17 sec were optimal.

Because the physical properties of silver electrodeposits are significantly improved by the codeposition of gallium, the alloy is used to improve the reliability of reed relay contacts.[1,2] To compensate for the 0.7-V difference[3,4] in the electrode potentials of silver and gallium in cyanide electrolytes, the plating bath must be prepared with a large concentration of gallium and a small concentration of silver. By using exponential current pulses, such as those in Fig. la, Viaczeslavov and Griekova[4,5] obtained good results. Favorable conditions for codepositing 14 percent gallium included a short decaying pulse from a high current (16 to 20 A/dm^2) during a time period of 0.23 to 0.25 see, followed by an off-period of 13 to 17 sec.[5] The electrical charge of each pulse was equal to 0.03 to 0.065 coulombs. However, the control of a specific alloy composition with such a current cycle is complicated and difficult. A conventional rectangular pulse (Fig. lb) was used during our study, instead.

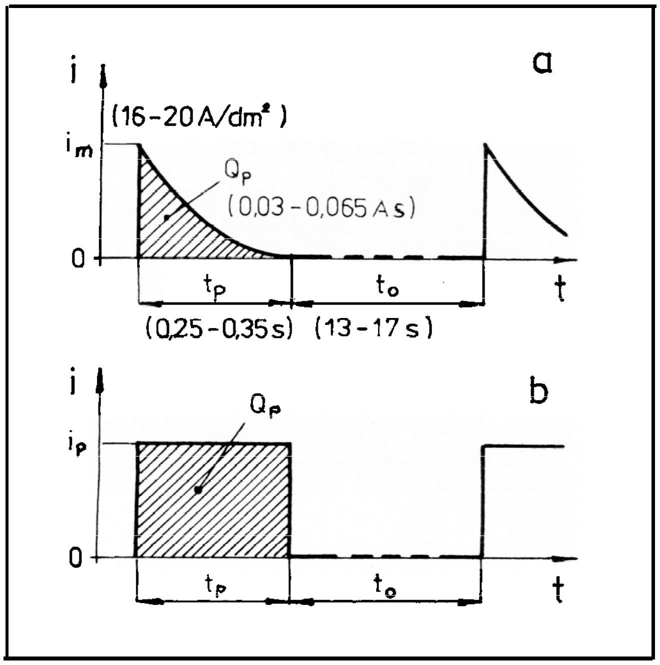
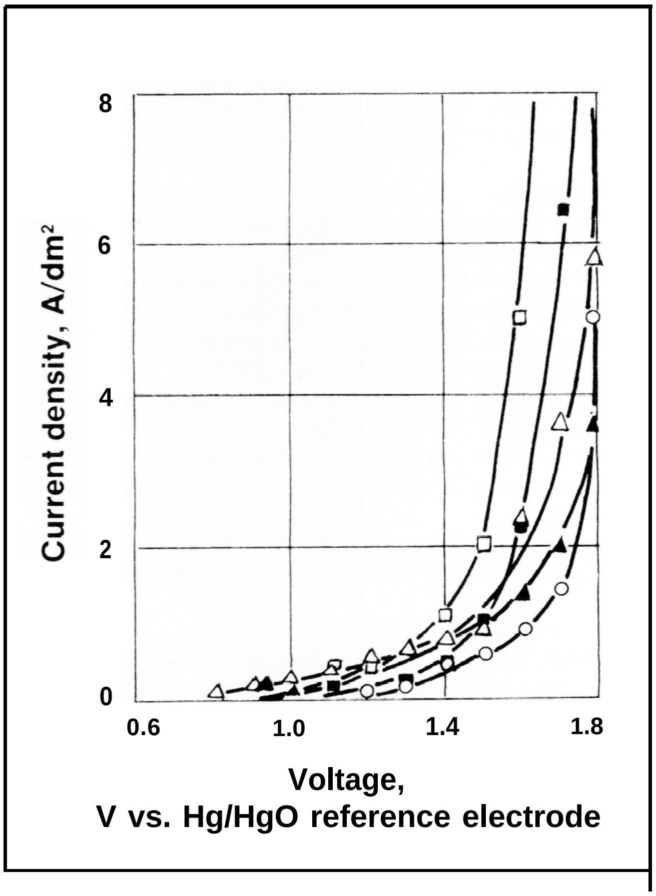


Fig. 1—Pulse cycles with a charge Q_p(a) an exponential shape and (b) a rectangular shape; t_p = pulse on-time, t_o = off-time.

Experimental Procedure

Potentiostatic studies included the cathodic polarization measurements shown in Fig. 2. The measurements were made with a potentiostat, a digital voltmeter, a platinum cathode with a surface area of 0.05 dm^2, and a silver or platinum counter electrode. Measurements referenced to a Hg/HgO electrode at a temperature of 20° C confirmed that the deposition potentials of silver and gallium differed considerably. To codeposit gallium and silver during subsequent experiments, solution constituents were maintained within the limits of 5 to 10 g/L silver, 40 to 50 g/L gallium, 70 to 80 g/L sodium cyanide, and 50 to 60 g/L potassium hydroxide; a sodium carbonate concentration of 30 g/L was adopted for all experiments.



for a bath-prepared with 10 g/L Ag and 70 g/L KCN. Closed triangles indicate a solution containing 10 g/L Ag and 80 g/L KCN. Open circles show data for a bath containing 40 g/L Ga and 55 g/L KOH. Open squares indicate points for a solution prepared with 10 g/L Ag, 40 g/L Ga, 75 g/L KCN, and 55 g/L KOH. The bath to develop closed-square data contained 5 g/L Ag, 40 g/L Ga, 75 g/L KCN, and 55 g/L KOH.

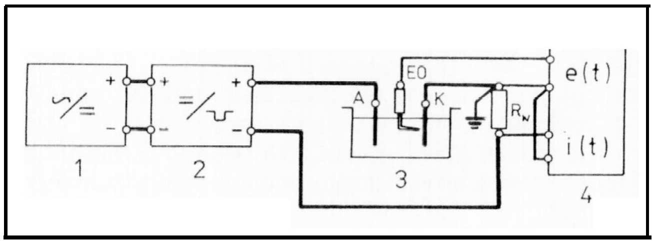


Fig. 3—The electrical system comprising(1) a constant current stabilizer; (2) the electronic pulse generator; (3) the plating cell; and (4) the two-channel oscilloscope.

To prepare a 600 mL plating bath, Ga$_2$O$_3$ was dissolved in a potassium hydroxide solution and mixed with a solution containing silver potassium cyanide and sodium cyanide. A copper cathode with an area of 0.09 dm^2 was placed between two silver anodes of the same area. The conditions for mechanical polishing, electrochemical cleaning and silver striking before silver alloy plating were detailed in a handbook.[6]

Figure 3 shows the electrical circuit for pulsed current plating. Integrating an electronic pulse generator with a transistor and a constant current stabilizer made it possible to select a current pulse value (I$_p$) up to 5 A, a pulse duration (t,) from 0.01 to 0.3 see, and an off-time (t$_o$) between pulses from 1 to 30 sec. An oscilloscope with a memory was used to screen the transient electrodeposition potentials. Solution temperature was 20 to 25° C, and total deposition time was 5 hr. Deposit thickness ranged from 10 to 20 µm.

Alloy deposits were examined visually before and after mechanical polishing. Soldering characteristics were determined in accordance with Polish Standard PN-70/T-04550. Adhesion was measured semiquantitatively by bending the plated copper sample 180° several times until the sample was permanently fractured. Deposit composition was calculated by weighing the sample before and after the deposit was dissolved in 30 volume percent nitric acid. The amount of silver in the sample was determined by titration. The gallium content was the difference between the weight of the deposit and the amount of silver.

Results and Discussion

Deposits obtained with a current density (i,) of 16 to 20 A/dm^2, an on-time (t$_p$) of 0.25 sec and an off-time (t$_o$) of 17 see, which had a gallium content of 6 to 10 percent, consisted of loosely coherent particles. This poor result was attributed to an excessive current charge that was greater than that used previously.[4]

The codeposition of gallium with silver requires a large shift in the cathode potential towards negative values that correspond to the limiting current density of silver. If the time required to remove silver ions from the diffusion layer at the start of each pulse is called the transfer time (t$_t$),[7] this transfer time for silver can be expressed as a function of the bulk concentration of silver ions, as follows:

$$t_t = \frac{(2F)^2 \times (C_{Ag})^2 \times D_{Ag}}{\quad} \tag{1}$$

where C$_{Ag}$ is the bulk concentration of silver, D$_{Ag}$ is the silver ion diffusion coefficient, F is the Faraday constant, and i$_p$ is the pulse current density.

Gallium is codeposited when t$_p$ is greater than the transfer time for silver. For practical use, t$_p$ should be much greater than the transfer time for silver.

In order to obtain sound, coherent deposits, the transfer time for silver plus the transfer time for gallium must be greater than the current pulse time (t$_p$). The transfer time for gallium is:

$$t_t = \frac{(2F)^2 \times (C_{Ga})^2 \times D_{Ga}}{2(i_p - i_L)^2} \tag{2}$$

where C$_{Ga}$ is the bulk concentration of gallium, D$_{Ga}$. is the gallium ion diffusion coefficient, and i$_L$ is the limiting current density for silver.

We assumed that the influence of natural convection on the transport process was negligible because the applied current parameters control diffusion layer thickness to values that could not be affected by convection. For practical reasons, we also assumed that the transfer time for silver should be in the range of 0.03 to 0.05 sec and conducted experiments with a pulse time (t$_p$) of less than 0.25 sec but greater than 0.1 see, while t$_o$ was 16 sec and i$_p$ was 18 A/dm^2. When t$_p$ was greater than 0.20 see, deposits were loose and powdery. However, when t$_p$ was less than 0.19 sec but greater than 0.10 see, deposits were adherent and compact, had a silver-like appearance, and were easily polished to a bright finish.

The influence of the pulse current density amplitude on the character of the deposit was investigated while t$_p$ and t, were constant at 0.15 and 16 see, respectively. The results confirmed that the favorable range of pulse current density was 16 to 20 A/dm^2. A higher current density produced powdery deposits. The influence of pulse current density on the gallium content of the alloy deposit is shown in Fig, 4.

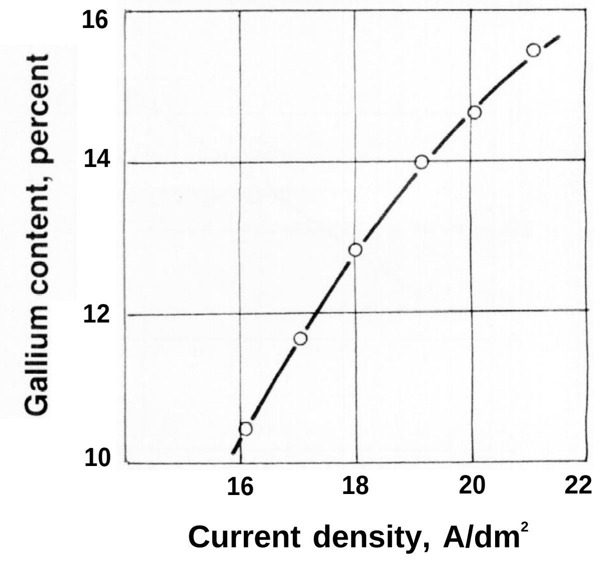


Fig. 4-The Ga content of the deposit as a function of the pulse current density (i$_p$). The Ga concentration in the bath was 50 g/L, on-time was 0.15 sec and off-time was 16 sec.

Prolonging the off time is favorable for increasing the gallium content of the alloy,' This trend was confirmed during our study with square pulses (Fig. 5). An off-time period (t,) of 13 to 17 sec proved favorable; prolonging the off-time had no effect on composition.

Comparison of the rectangular pulse (Fig. 1 b) and the exponential pulse (Fig. 1a) shows that the rectangular pulse produces a higher charge when both have the same frequency. The square pulse speeds up the plating process four or five times, however.

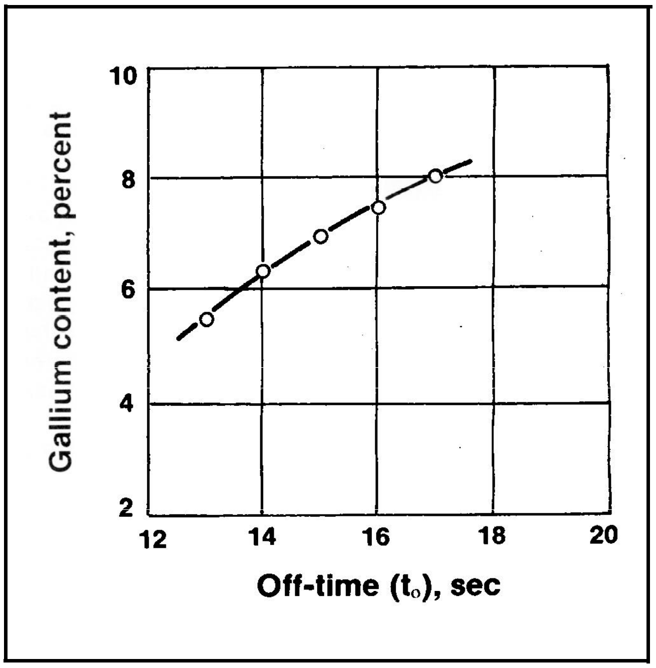


Fig. 5—The Ga content of the deposit as a function of the off-time (t_o). The Ga concentration in the bath was 40 g/L, the pulse on-time was 0.15 sec and the pulse current density was 18 A/dm^2.

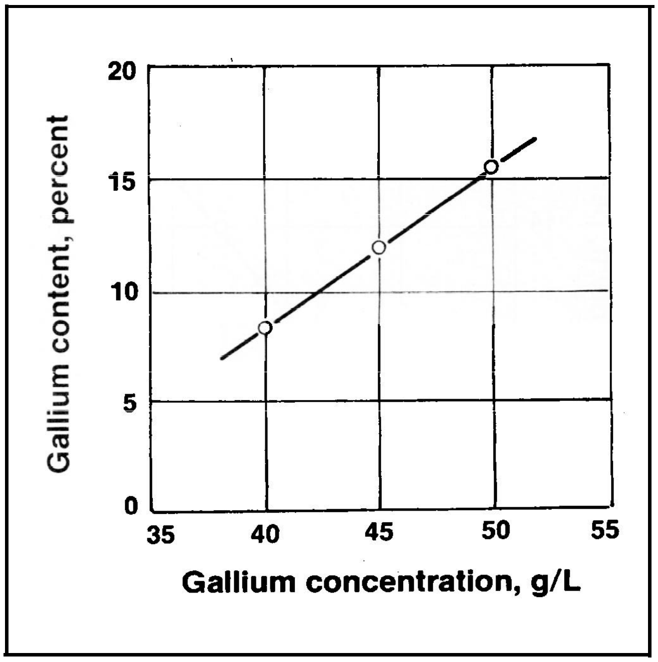


Fig. 6—The Ga content of the deposit as a function of Ga concentration in the bath. Pulse on-time was 0.15 sec, pulse current density was 20 A/dm^2, and the off-time was 16 sec.

Figure 6 shows the effect of increasing the gallium concentration in the alloy plating bath, when i_p was 20 A/dm^2, t_p was 0.15 sec, and t_o was 16 sec. The gallium content of the deposit approximately doubled when the gallium concentration was increased from 40 to 50 g/L while i_p was 20 A/dm^2, t_p was 0.15 sec and t_o was 16 Sec. Deposits produced with these conditions met requirements for quality.

Conclusions

Rectangular pulses produced bright, silvery deposits that were easy to polish when the pulse time was less than 0.19 sec but above 0.10 see, the off-time ranged from 13 to 17 sec and the pulse current density was 16 to 20 A/dm^2. The gallium content of the deposit increases with an increase in the pulse current density, the duration of off-time or an increase in the gallium concentration in solution. Gallium contents ranged from 1.0 to 15.4 percent during our study. With favorable pulsed current parameters, rectangular pulses deposit silver-gallium alloy much faster than exponential pulses.

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