Pulse-Plating of Gold-Copper-Cadmium Alloys

Ulrike Fastner, Selma Hansal CEF-3, Wolfgang E. G. Hansal CEF-3

Center for Applied Electrochemistry, Wiener Neustadt, Austria

Abstract:

Layers produced with Pulse Plating show at least the same surface properties as layers produced with direct current, such as smoothness, wear- or corrosion resistance. In most cases, pulse plated layers equal the properties of direct current layers even at a lower layer thickness.

In this work, the influence of pulse plating without off-time (t_{off}) was examined. This means, that based on direct current, current pulses were applied on highly polished copper substrates. In a second step, the direct current density was varied and it's influence on roughness and grain size of the resulting gold copper cadmium layer was examined.

For more information, contact:

Dr. Wolfgang E. G. Hansal, CEF-3

Center for Applied Electrochemistry
Viktor Kaplan Straße 2
2700 Wiener Neustadt
Austria / Europe

Phone: +43-2622-22266-42
FAX: +43-2622-22266-50
e-mail: wolfgang.hansal@echem.at

Introduction:

Gold and gold layers are widely used; as well for costume jewellery[1] and decorative purposes as for electronic applications[2]. The reason for the wide field of applications of gold layers can be found in its´ outstanding properties: excellent corrosion resistance, low electrical resistivity, solderability, weldability and gloss.
Since gold and gold alloys are high cost materials, any measure of reducing the amount of gold necessary is highly welcome.
A possibility is alloying the gold layer with less expensive metals e.g. copper, nickel, cobalt or silver. Additionally, the use of gold alloys allows to increase and adjust the hardness[3,4] or the color of the deposited layer. Usually, gold alloys have Knoop hardness numbers (KHN_{25}) ranging from 140 to 250, whereas soft gold layers deposited at conventional current densities show hardness numbers between 40 an 90 (KHN_{25})[5]. The color of the deposited layer can range from whitish (Ni, Pd), over greenish (silver) to reddish (copper)[6], depending on the alloying metal.
Another possibility to reach this aim is Pulse Plating. Layers produced using Pulse Plating, exceed layers deposited by direct current in density due to the smaller grain size of the deposited gold. Therefore thinner layers, providing at least the same surface properties like smoothness, reflectivity, wear- and corrosion resistance, can be produced.
The combination of alloy plating with Pulse Plating merges all the mentioned advantages: while adjusting the hardness and the color of the deposited layer and producing very dense, smooth and small grain sized layers, cost intensive excessive gold can be spared.
In the present work, gold alloys were deposited using pulsed current. The influence of the pulse frequency on the surface roughness and the grain size of the deposited layer was investigated. In a second step a direct current was superimposed to the pulse sequence and again, surface roughness and grain size were examined.

Experimental:

Highly polished copper platelets (99,99%) were used as substrates and degreased in 10vol% sulfuric acid before plating. For all galvanic depositions, a common cyanidic gold copper cadmium bath was used. The bath temperature was kept constant at 70°C (158°F), during the deposition, the bath agitation was provided by mechanical stirring. Anodes were made of platinized titanium and positioned parallel to the cathode surface at a distance of four centimeters.
As pulse rectifier, a JAISSLE Potentiostat/Galvanostat IMP 83PC – 10 was used. This device was controlled and the resulting data were evaluated using the software package ECMWIN (IPS Schrems). Additionally, a function generator (HAMEG Funktion Generator HM 8131-2 combined with a HAMEG Analog Digital Scope HM 1507-2) was used for applying 500 Hz Pulses.
Several pulse sequences were developed and tested, varying the pulse frequencies within a range between 0,5 and 500 Hz. The average current densities ranged from 0,3 A/dm² to 0,525 A/dm².
Table **1** gives an overview over the experimental details. Starting from a “normal” pulse plating sequence, we additionally applied a base current. This results to a pulse sequence

without real off time, as schematically shown in Figure 1. The applied direct current densities used varied from 0,15 A/dm^2 to 0,45 A/dm^2.

Table 1: Overview of the experimental details.

Sample Nr.	Direct current density [A/dm^2]	Peak current density [A/dm^2]	**Frequency** [Hz]
1	0	0,6	0,5
2	0	0,6	5
3	0	0,6	50
4	0	0,6	500
5	0,15	0,6	0,5
6	0,15	0,6	5
7	0,15	0,6	50
8	0,15	0,6	500
9	0,2	0,6	0,5
10	0,2	0,6	5
11	0,2	0,6	50
12	0,2	0,6	500
13	0,3	0,6	0,5
14	0,3	0,6	5
15	0,3	0,6	50
16	0,3	0,6	500
17	0,45	0,6	0,5
18	0,45	0,6	5
19	0,45	0,6	50
20	0,45	0,6	500

Environmental scanning electron microscope (ESEM) pictures were made with a PHILIPS XL 30 ESEM-FEM evaluating the structure and the average grain size of the deposited gold alloy layers. The surface roughness was measured by atomic force microscopy (AFM) using an ATOS EXPLORER. All samples were etched with a "GATAN Model 682" etching system before ESEM pictures were taken, using a beam energy of 7 keV and 5 min etching time.

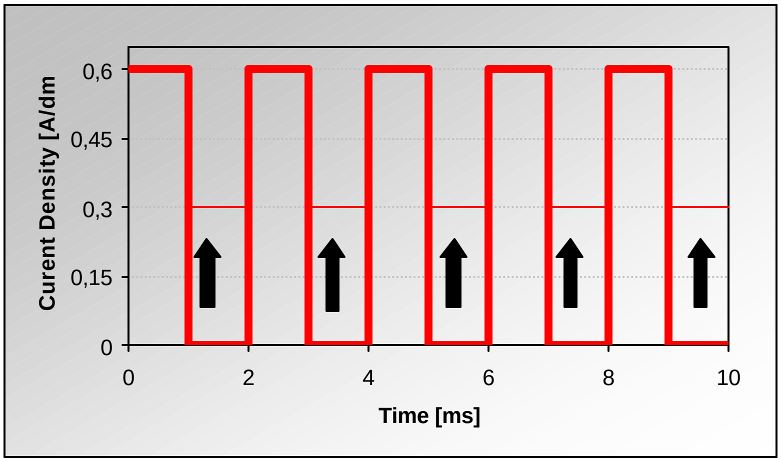

Figure 1: Scheme of the pulses used in this work: Beginning with a normal pulse sequence (bold line), we additionally applied a base current density leading to a pulse sequence without off-time.

Results and Discussion:

The average layer thickness was kept constant at approximately 3 micrometers, by adjusting the plating time for each average current density. The resulting gold alloy layers were homogenous, single layers. Figure 2 shows a representative ESEM picture of a cross section of a deposited gold alloy layer.

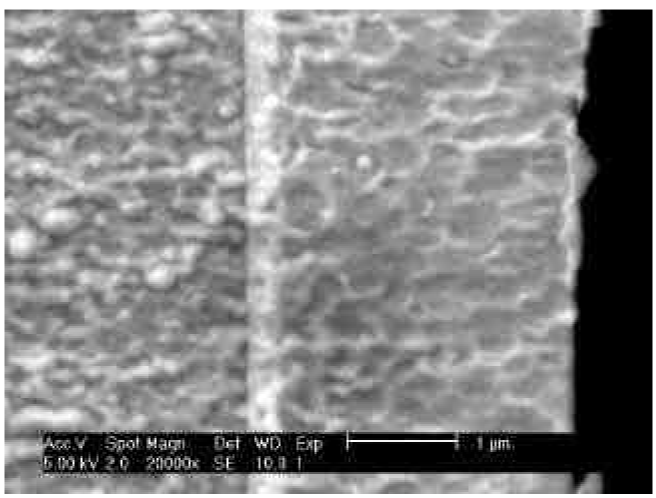

Figure 2: Cross section of a deposited gold alloy layer. The layer on the right is the plated gold alloy, on the left side, the copper substrate can be seen.

INFLUENCE OF PULSE FREQUENCY ON GRAIN SIZE AND SURFACE ROUGHNESS

Pulse depositions were performed in order to investigate the influence of the pulse frequency on the average grain size and the surface roughness.

Table 2 summarizes the results for the measured grain sizes for the respective frequencies.

Table 2: Dependency of the grain size on the applied pulse sequence.

Base current density	0 A/dm²	0,15 A/dm²	0,2 A/dm²	0,3 A/dm²	0,45 A/dm²
Frequency [Hz]	Grain Size [nm]				
0,5	115	114	111	112	117
5	96	94	91	93	100
50	92	90	88	90	98
500	88	85	83	84	98

In all cases, the grain size is reduced with increasing pulse frequency. These results are in good accordance with literature[7].
It was found, that the average grain size does not decrease linearly with pulse frequency. A remarkable decrease of the average grain size was observed when the frequency was changed from 0,5 to 5,0 Hz, independent on the level of base current density. At higher frequencies just minor changes of the average grain size were observed. Nevertheless, the smallest grain sizes were found at the highest pulse frequencies, independent on the level of base current density. Figure 3 gives a graphical survey over the measured grain sizes.

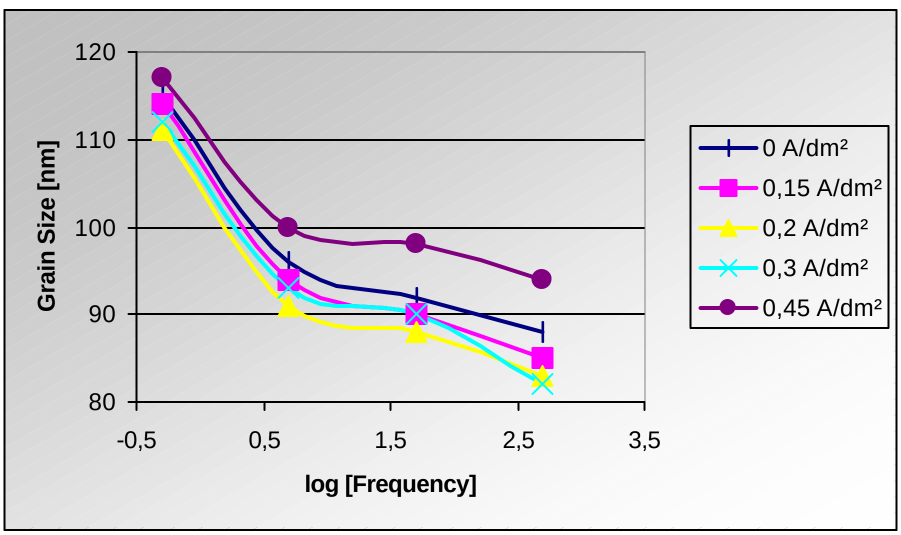

Figure 3.: Dependency of the average grain size on the frequency of the pulses for different levels of applied base current density.

Figure 4 shows two representative ESEM pictures of deposited gold alloy layers. The left layer was produced with a pulse frequency of 0,5 Hz, the right picture shows an ESEM

Picture of a layer produced with a pulse frequency of 50 Hz. The applied base current density was for both samples of 0,15 A/dm².

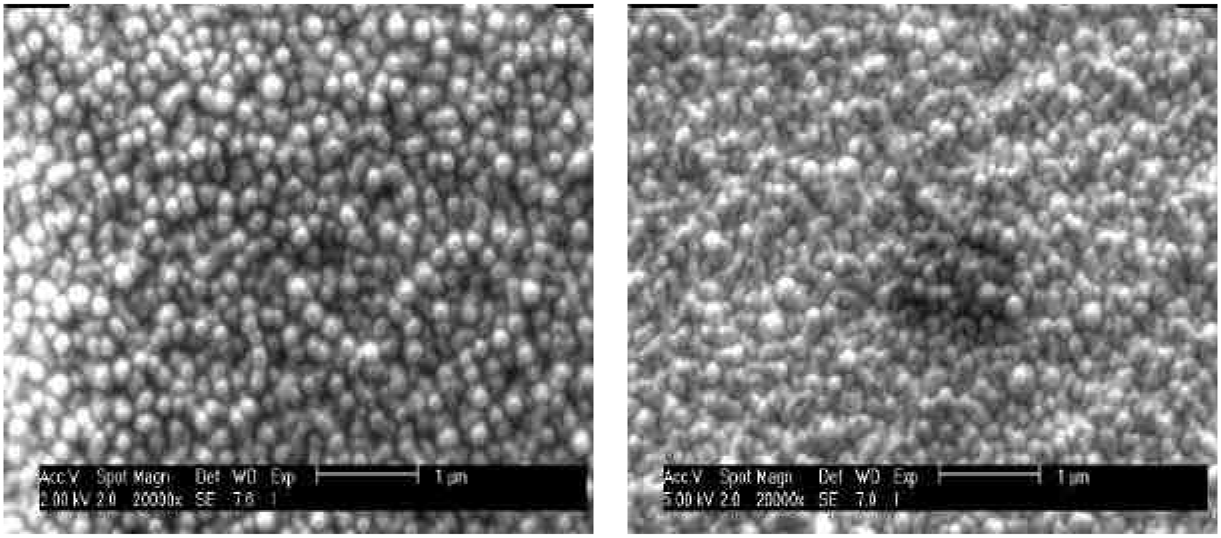

Figure 4: The layer depicted in the left ESEM picture was produced with a pulse frequency of 0,5 Hz, the layer depicted in the right picture shows an ESEM Picture of a layer produced with a pulse frequency of 50 Hz. The base current density was for both depositions 0,15 A/dm² (Factor of Magnification is in both Pictures 20.000x).

The influence of the pulse frequency on the surface roughness of the produced layers was also determined. The obtained results are listed in Table 3.

Table 3: Dependency of the grain size on the pulse frequency.

Base current density	0 A/dm²	0,15 A/dm²	0,2 A/dm²	0,3 A/dm²	0,45 A/dm²
Frequency [Hz]	Roughness [nm]				
0,5	26	25	20	24	31
5	20	20	15	17	25
50	10	8	7	8	14
500	17	16	13	16	18

Similar to the tendency found for the grain size a decrease in surface roughness with increasing pulse frequency was measured. Up to a pulse frequency of 50 Hz a almost linear dependency of the average surface roughness on the pulse sequence was observed. A further increase of the pulse frequency leads again in all cases investigated to an increase in surface roughness. The reason for this behavior might be the content of organic additives within the bath. Since these additives increase the viscosity of the bath, the deposition at high pulse frequencies could be hindered, reducing the positive effects of the pulse deposition.

INFLUENCE OF THE OVERLAYING DIRECT CURRENT DENSITY ON GRAIN SIZE AND SURFACE ROUGHNESS

Using Pulse Plating with an additionally applied base current density gives interesting effects on the grain size of the resulting gold alloy layer as well as on the average surface roughness. A deposition using a “normal” pulse plating sequence with no applied base current density leads to layers exhibiting a relatively low average grain size. When a base current density is added to the pulse sequence, a change in grain size could be measured. A decrease of the average grain size was determined for all levels of base current density. The average grain sizes decreased with increasing base current densities, up to a minimum of grain size at approximately 0,2 A/dm². A further raise of the base current density is followed by an increase of the grain size. The reason might be that the deposition becomes too similar to direct current plating when a high base current density is applied.

Figure 6 shows the influence of the applied base current density on the surface roughness. The higher the level of base current density, the smoother is the resulting gold alloy surface. The surface roughness decreases with the level of base current density up to 0,2 A/dm². At higher levels of base current density, the surface roughness slightly increases again. This result is in good accordance with the increase of the grain size at high levels of base current density and can be explained by the increasing similarity of the pulse sequence to direct current plating. Figure 5 shows two representative AFM micrographs of gold alloy layers deposited at different levels of base current density. The micrograph on the right side of Figure 5 shows a pulse plated surface without any base current density, the micrograph on the left side a surface layer deposited with an additionally applied base current density of 0,3 A/dm². The pulse frequency was 50 Hz for both samples. Roughness measurements indicate a decrease from 14 nm for the surface layer deposited without base current density to 8 nm for the gold alloy layer deposited with an applied base current density.

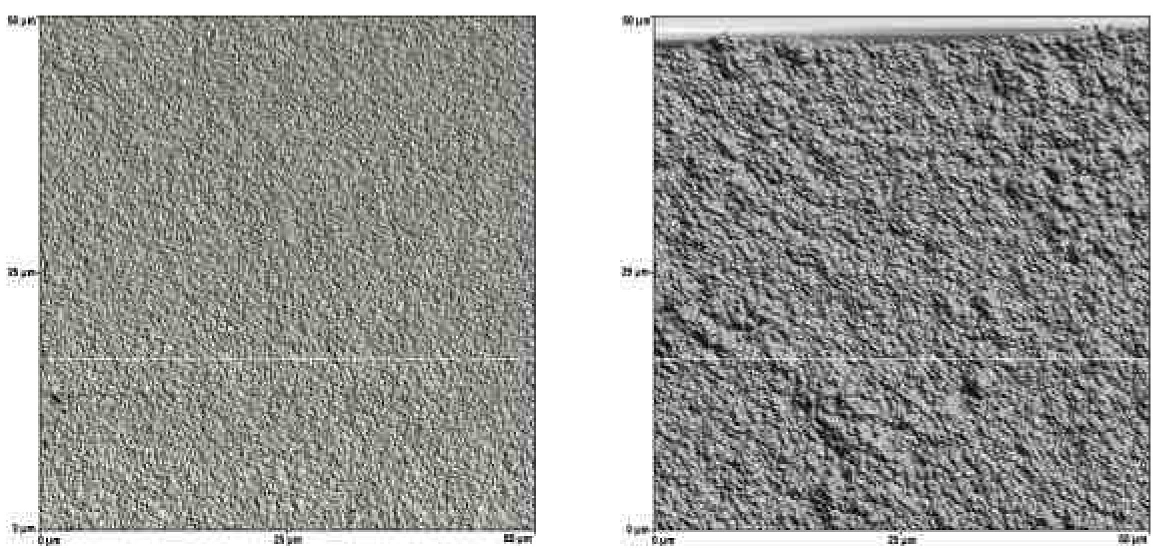

Figure 5: Influence of the base current density on the surface roughness: right side: pulse sequence without any base current density, left side: deposited with a base current density of 0,3 A/dm². The

surface roughness decreases from 14 nm to 8 nm when the base current density is applied (pulse frequency 50 Hz for both samples)

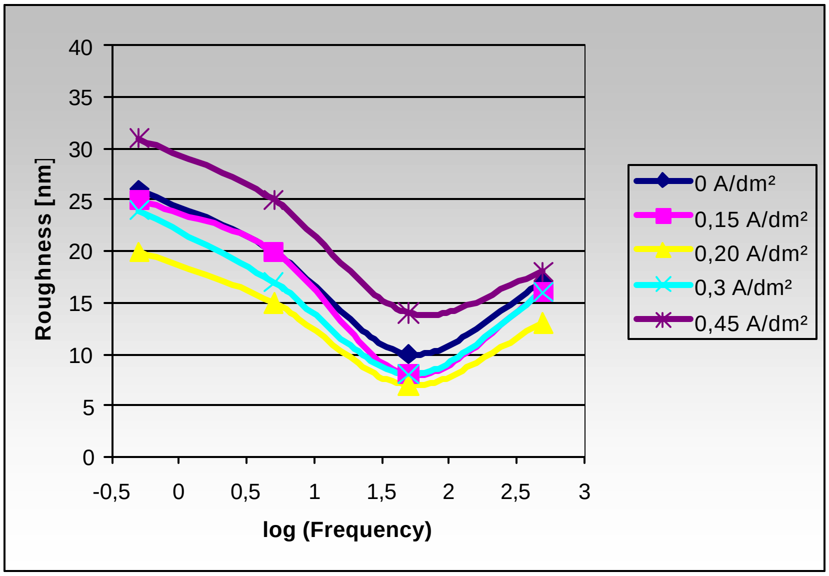

Figure 6: Dependency of the surface roughness on the deposition frequency and the level of base current density.

Conclusion:

The influence of the pulse frequency with and without superimposed base current on the grain size and the surface roughness was investigated. Gold alloy layers were plated achieving a minimum surface roughness of 7 nm and exhibiting lowest grain sizes of 83 nm. As generally known, the grain size was decreased applying a higher pulse frequency. Although this relation is not linear the grain size is always lower at higher pulse frequencies. The phenomenon is explainable with the higher nucleation rate with higher pulse frequencies.

A further decrease of grain size was observable by applying a base current to the pulse sequence. The effect of decreasing grain size with different base current density does not exceed a certain maximum of base current density. A further increase in base current density leads again to an increase in grain size leading to slightly higher grain sizes than without applying a base current, approaching conditions like at direct current plating. This phenomenon is probably correlateable to an occurring mass transport effect at current densities lower than the proper deposition current density. A migration towards the cathode is constantly provided, without reducing the metal ions to be plated, below the current density of 0,3 A/dm². The thickness of the diffusion layer at the cathode surface is lower since the vicinity of the cathode surface is enriched by active cations. When the next pulse occurs more cations are available for deposition. A higher nucleation rate is the result, leading to smaller grain sizes and smoother surfaces. By increasing the base current density to values higher than a third of the peak current density of the pulses, gold alloy is constantly plated leading to an increased surface roughness and higher average grain sizes.

Acknowledgement:

This work was supported by the Kplus program of the Austrian government. The authors also wish to express their thanks to the scientific director of the Center for Applied Electrochemistry, Dr. G. E. Nauer, for supporting this work.

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