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GOLD PLATING

PDO 6984761, Final Report

C. J. Stimetz, Project Leader

Internal Distribution March 1973

Prepared for the
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**Kansas City
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Project Leader:
C. J. Stimetz
Department 814

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Final Report

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GOLD PLATING

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Prepared by C. J. Stimetz, D/814, under PDO 6984761

The purity and microhardness of gold deposits from nine different gold plating solutions were determined. In general, these solutions gave soft high-purity gold deposits. A study was conducted on these solutions to determine the effects of metallic contamination on the purity and microhardness of the gold deposits.

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SUMMARY

Nine gold plating solutions, both proprietary and nonproprietary, were investigated for their ability to produce soft, high-purity electrodeposits. The purity of the gold deposits obtained from these solutions was greater than 99.9 percent, with cathode efficiencies of 94 percent or better. Microhardness measurements were slightly higher than those reported by the vendors.

The gold solutions were purposely contaminated with nickel, copper, cobalt, iron, and cadmium at a concentration of 10 milligrams per liter. Gold deposits obtained from these solutions were investigated to determine their purity, microhardness, and solderability. Five of the nine gold solutions that were contaminated gave deposits with a purity of 99.9 percent. From the analyses of these deposits, codeposition of a nickel and cobalt does not seem to be a problem in any of the gold solutions. Iron and copper codeposition varies from significant to negligible. Cadmium codeposition with gold was notable in all the solutions. ACR 24Kt and Pur-A-Gold 130 gold plating solutions were the least sensitive to codeposition of metallic impurities. Although soft gold deposits were obtained from ACR 24Kt, the microhardness of deposits from Pur-A-Gold 130 was slightly higher than 90 Knoop.

Not much difference was observed in the microhardnesses of the gold deposits from the contaminated and pure solutions. In a few cases where the degree of contamination of the gold deposit was notable, an increase in the microhardness occurred.

The solderability of all the gold deposits was good from either pure or contaminated solutions.

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DISCUSSION

SCOPE AND PURPOSE

High purity gold electrodeposits are required on future hybrid microcircuits. These deposits must have a purity greater than 99.9 percent and a Knoop hardness of 90 or less. Nine gold plating solutions, proprietary and non-proprietary, were evaluated under limited production conditions for their ability to produce this type of deposit.

ACTIVITY

The gold solutions investigated and some of the more important operating parameters are listed in Table 1.

Table 1. Properties of Gold Solutions

Vendor	Gold Solution	Gold Concentration (g/l)	Operating Temperature (°C)	pH
Technic *	Orotemp 24	8.2	62	6.2
Dequest 2041	Nonproprietary	12.3	60	6.0
Sel-Rex **	Pur-A-Gold 125	8.2	60	5.8
Sel-Rex **	Pur-A-Gold 130	8.2	60	5.8
Sel-Rex **	Temperex HD	8.2	65	4.4
Sel-Rex **	BDT-200	12.3	50	9.5
Lea-Ronal ***	Aurall 292M	8.2	72	7.0
Engelhard †	E-50	12.3	70	6.4
American ††	ACR 24Kt Neutral Gold 403	8.2	70	8.0
* Technic Incorporated, Providence RI ** Sel-Rex Corporation, Nutley NJ *** Lea-Ronal Incorporated, Freeport NY † Engelhard Minerals and Chemicals, Newark NJ †† American Chemical and Refining, Waterbury CT				

Determinations and Studies of Gold Deposits

The purity, solderability, and microhardness of the deposits from these solutions were determined. Cathode efficiencies were also measured. After contaminating these solutions, the deposits were re-evaluated.

A working volume of one liter of gold solution was used in all the tests. After checking and adjusting the pH of the solution, it was placed in a constant temperature bath that was controlled to $+1^{\circ}\text{C}$. Platinized titanium mesh anodes were used. Rotation of the cathode was used as agitation, and all plating was done at a current density of 3 amp/ft^2 (3.23 mA/cm^2). At no time was the gold content of the bath allowed to fall more than 15 percent of the initial gold concentration.

For the determination of the purity of the deposit, a passivated stainless steel rod 0.375 inch (9.5 mm) in diameter and 6 inches (152 mm) long was used. The rod was weighed, plated, and then reweighed. The weight of the gold deposit, usually about 500 mg, and the ampere minutes of plating time are used to calculate the cathode efficiency. After peeling the gold from the stainless steel rod, the gold was analyzed for metallic impurities by emission spectroscopy. In some cases atomic absorption spectroscopy was used to substantiate the emission spectroscopy results.

Solderability dip tests were performed on gold that was deposited on 0.04-inch (1 mm) diameter copper wire. Thicknesses of the gold deposits ranged from 0.00005 inch to 0.00015 inch (0.00127 mm to 0.0038 mm). The dip test was 4 seconds in tin-lead solder (63/37 percent by weight) at 230°C using Alpha 100-30 nonactivated rosin-based flux. After the dip test, the specimens were examined at 10X magnification to determine solderability. The criteria for solderability are defined by MIL-STD-202, Method 208.

Microhardness tests were performed on gold deposited on 0.375-inch (9.5 mm) diameter copper rod. The gold deposit was overplated with copper. To determine the Knoop hardness, a cross section was taken and indentations were made 90° apart with the long dimension of the indentation perpendicular to the radius of the cross section. A 25-gram load that required a thickness of 0.002 inch (0.051 mm) of gold was used.

A metallic contamination study was conducted on all the gold plating solutions. The contaminants investigated were iron, copper, nickel, cobalt, and cadmium. Introduction of these impurities into fresh gold solution was achieved by adding measured amounts of the following salts to each gold solution.

- Iron (III) Chloride $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$
- Copper (II) Nitrate $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$

- Nickel (II) Nitrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
- Cobalt (II) Sulfate $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$
- Cadmium Nitrate $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$

Appropriate quantities of these salts were added to the solutions to achieve a concentration of about 10 mg/liter (0.01 kg/m³).

Some of the gold solutions investigated contained chelates which complex with metallic impurities commonly found in gold plating solutions. Chelates prevent the codeposition of other metals with the gold. In general, gold solutions containing chelates should be more reliable in producing high-purity gold deposits than the solutions without chelates. Table 2 lists the gold solutions evaluated.

Table 2: Chelates in Gold Solutions

With Chelates	Without Chelates
Orotemp 24	ACR 24Kt
Pur-A-Gold 130	Pur-A-Gold 130
Aurall 292M	BDT-200
Dequest 2041	Temperex HD E-50 Acid Gold

All of the gold deposits obtained from the pure solutions had a purity of 99.9+percent. In these deposits, the only appreciable contaminant was silver. Cathode efficiencies for each plating bath are shown in Table 3.

Measured amounts of nickel, copper, cobalt, iron, and cadmium were added to the gold solutions. In Table 4 the concentrations (in mg/liter) of these impurities in the various gold solutions are shown.

Deposits obtained from the contaminated gold solutions were tested to determine their purity, solderability, and hardness.

The detailed results from the analysis of these deposits are listed in Table 5 and the methods of investigation for each determination are described on Page 15. Codeposition of nickel and cobalt at these concentrations doesn't seem to occur in any of the gold solutions. Iron was significantly

codeposited with gold in the BDT-200 solution. Copper codeposition with gold was extensive in Dequest 2041, Aurall 292M, and BDT-200. To a lesser degree copper was also a problem in Temperex HD, E-50 Acid Gold, and Orotemp 24. In all the solutions investigated cadmium codeposition with gold was significant.

From the trace element analysis of the contaminated gold deposits, the purities can be calculated. In Table 6 a comparison of the purity of gold deposits from pure and contaminated solutions is shown. Pur-A-Gold 130 and ACR 24Kt appear to be the least sensitive to codeposition of metallic impurities.

Table 3. Cathode Efficiencies of Pure Gold Solutions

Solution	Cathode Efficiency (Percent)
Temperex	96.96
BDT-200	98.77
Dequest 2041	94.12
Orotemp 24	94.87
Pur-A-Gold 125	95.36
Pur-A-Gold 130	97.25
ACR 24Kt	98.41
E-50 Acid Gold	95.97
Aurall 292M	99.80

Solderability of all the gold deposits was good whether the deposits were obtained from pure or contaminated solutions.

The Knoop hardness was determined for gold deposits from the pure and contaminated solutions (Table 7).

In general the Knoop hardness values were slightly higher than those reported by the vendors. Soft gold deposits, 90 Knoop or less, were the type of deposits expected from the pure solutions with the exception of BDT-200 which gave harder deposits (140 to 160 Knoop). The Knoop hardness exceeded 90 in the gold deposits obtained from Dequest 2041 and Pur-A-Gold 130.

In three cases the microhardness is significantly lower for the deposits obtained from the contaminated solutions of ACR 24Kt, Orotemp 24, and Pur-A-Gold 125 than from the corresponding pure solutions. This is unusual, as contamination should increase the microhardness. The divergence of these results could be attributed to the conditions under which the microhardness tests were performed. A 25-gram load was chosen since this is the standard load used by the vendors of gold plating solutions. However, the reproducibility of the indentation is subject to a wide variation with this light load. Another problem was that the microhardness tester used in the laboratory had a minimum recommended load of 25 grams; operation at the minimum load rating led to some inaccuracy.

Table 4. Concentration of Contaminants in the Gold Plating Solutions in Milligrams Per Liter

Solution	Ni	Cu	Co	Fe	Cd
Dequest 2041	9.92	10.6	10.5	10.6	10.7
Orotemp 24	9.73	9.37	10.3	9.69	8.66
Aurall 292M	9.16	9.68	9.76	9.70	9.82
E-50 Acid Gold	9.61	10.6	11.0	10.7	12.0
ACR 24Kt	9.61	11.2	10.3	10.4	11.5
Pur-A-Gold 130	10.3	10.1	10.3	11.0	10.7
Pur-A-Gold 125	10.4	10.1	10.4	11.0	10.6
BDT-200	11.1	11.0	10.3	10.4	10.3
Temperex HD	9.81	10.0	10.2	10.6	11.1

Test Methods (Corollary With Table 5)

Purity of the Deposit

The stainless steel mandrel pretreatment included these steps:

- Polishing with Polierpaste Supfina and cleaning with acetone;
- Immersion for 2 minutes in Oakite 191 at 80°C; and
- Soaking for 20 minutes in a passivation solution at 50°C.

the composition of the passivation solution was 22.5 g/l of sodium dichromate dissolved in a 1:4 concentration of nitric acid in deionized water to make one liter of solution.

Solderability and Hardness Specimen

The pretreatment of copper wire and/or rod consisted of these steps:

- Acetone wipe;
- Immersion for 2 minutes in Oakite 191 at 80°C;
- Immersion for 30 to 60 seconds in ammonium persulfate solution (240 g/liter);
- Immersion for 30 to 60 seconds in 10 volume percent sulfuric acid; and
- Immersion for 15 to 20 seconds in copper - bright dip.

The composition of the copper bright dip (in ml) was sulfuric acid 444; nitric acid 222; water 332; and 2 of hydrochloric acid.

Table 6. Percent Purity of Gold Deposits

Solution	Pure	Contaminated
ACR 24Kt	99.985	99.978
Aurall 292M	99.995	99.924
Dequest 2041 *	99.995	99.843
Orotemp 24 *	99.991	99.886
E-50 Acid Gold *	99.991	99.895
Pur-A-Gold 125	99.989	99.915
Pur-A-Gold 130	99.988	99.993
Temperex HD	99.994	99.915
BDT-200 *	99.994	99.801
* Fell below the 99.9 percent minimum.		

Table 7. Knoop Hardness of Gold Deposits

Solution	Pure	Contaminated
E-50 Acid Gold	67	69
Dequest 2041	93	127
ACR 24Kt	86	54
Aurall 292M	76	78
Orotemp 24	60	48
Pur-A-Gold 125	84	74
Pur-A-Gold 130	94	101
BDT-200	141	174
Temperex HD	61	70

ACCOMPLISHMENTS

Nine gold plating solutions were evaluated for their ability to produce high-purity soft gold deposits under production conditions. The ACR 24Kt and Pur-A-Gold 130 gold plating solutions appear to be the least sensitive to codeposition of metallic impurities. However, the microhardness of the gold deposits from the Pur-A-Gold 130 was slightly higher than 90 Knoop. Aurall 292M, Pur-A-Gold 125, and Temperex HD gave softer deposits than ACR 24Kt and Pur-A-Gold 130 but they codeposited metallic impurities more readily.

The results of this investigation indicate that the Pur-A-Gold 130 and ACR 24Kt gold solutions offer some advantages over the Temperex HD gold solution currently used in production to produce soft, high purity gold deposits.

FUTURE WORK

In this investigation only the short term operating effects of these gold solutions were considered. If either the ACR 24Kt or the Pur-A-Gold 130 solution were to be considered for production use, the longer-term operating effects such as bath life need to be studied. For microelectric applications, the bonding characteristics of these gold deposits need to be determined. No additional activity is planned at this time.