## A Versatile Non-Cyanide Gold Plating System

By Ronald J. Morrissey

A sulfite gold plating solution is capable of stable operation at pH values as low as 4.0. At pH values lower than about 6.5, sulfur dioxide is released at a controlled rate during operation. Excess sulfite is consequently released from the solution, which allows the specific gravity to be maintained in protracted operation, and minimizes formation of sulfate. The solution is operable with various metallic and organic brighteners. The effects of several such brightener systems on deposit grain size, crystal orientation, leveling and porosity vs. thickness are presented.

ommercial sulfite gold plating solutions were first developed in the early to middle 1960s.<sup>12</sup>Gold is deposited from the sulfite complex according to

$$M_aAu(SO_a)_a + H_aO + e^- \rightarrow Au^0 + M_aSO_a + MHSO_a + OH^-$$
 (1)

where M is an alkali metal or ammonium ion. The sulfite ion is itself in equilibrium with sulfur dioxide according to

$$SO_3^{2-} + H_3O \leftrightarrow SO_3(g) + 2OH^-$$
 (2)

Because reaction (2) forms hydroxyl ions, the equilibrium is pH-dependent, and the sulfite ion is ordinarily stable only at alkaline pH. As originally configured, sulfite gold plating solutions operated at pH values above about 9.5. Most commercially available solutions still do so.

There have been numerous attempts to reduce the operating pH of sulfite gold solutions. Meyer et al.<sup>3</sup> claimed that in the presence of organic polyamides, notably ethylenediamine, sulfite gold solutions could be operated at pH values as low as 6.5. Similarly, Laude et al.<sup>4</sup> claimed that even in the absence of polyamides, solutions based on ammonium gold sulfite could be operated at pH 6 to 8. In practice, **however, commercially available** solutions, even with additive systems, have tended to operate only at pH values above about 7.5.

The gold sulfite complex contains two sulfite ions per gold ion. At alkaline pH, sulfite ions accumulate in the solution as gold is replenished, and it is characteristic of such solutions that the specific gravity tends to increase continually as they are operated, This characteristic is highly undesirable for high speed operation, or for applications requiring selectivity. It would clearly be desirable to operate a sulfite gold solution under conditions such that sulfur dioxide is volatilized at approximately the same rate at which gold is plated out. Such solutions would tend to be self-regulating, and would operate in a fashion analogous to that of the neutral and acid cyanide gold solutions widely available.

In this paper, a stabilized sulfite gold system is described which is capable of controlled operation at pH values as low as 4.0.<sup>5</sup>The operating characteristics of the solution and some physical properties of deposits obtained from it are examined.

#### Solution Operation

As currently configured, the electroplating solution operates in the pH range of about 6 to 7. The electrolyte system is based on sodium sulfite and organic polyacids. A summary of recommended operating conditions for this system is shown in Table 1. Current efficiencies exceeding 100 percent are sometimes encountered in plating from sulfite gold solutions. It has been theorized that degradation products, such as thiosulfate and tetrathionate act to catalyze the decomposition of sulfite ion.<sup>4</sup>

In the pH range of 6 to 7, the solution is approximately selfregulating with respect to sulfite content. Experience with this system over somewhat more than one year indicates that solution pH and sulfite content both tend to decrease slowly (over intervals of months) if the gold content is adjusted only infrequently, but to remain approximately constant if frequent gold additions are made. At pH values above about 5.5 there is no detectable evolution of sulfur dioxide as the solution is operated. Below pH 5.0, evolution of sulfur dioxide becomes rapid. Under these conditions, the solution must be vented and replenished frequently with sulfite. For ordinary purposes, the free sulfite content of the solution is maintained at 30 to 45 g sodium sulfite/liter. The solution will function satisfactorily at sulfite levels as low as 10 g/L at pH 6 to 7.

Figure 1 a shows a Hull Cell panel plated from the sulfite gold solution without brightening agents. The gold content of the solution was eight g/L and the Hull Cell was operated at 0.5 A for five min at 60 °C. The deposit is essentially specular at current densities up to about 8 mA/cm<sup>2</sup> and semi-bright to about 15 mA/cm<sup>2</sup>. Addition of 30 ppm arsenic (Fig. 1 b) extends the

 Table 1

 Recommended Operating Conditions

Tankage:	Polypropylene, Fiberglass, Plastic-Lined Steel, or Glass.					
Anodes:	Platinized. Anode-to-cathode area ratio should beat least 1:1.					
Heaters:	Titanium, Teflon, Alumina or Quartz. Low power density heaters are preferred. Localized boiling of the solution should be avoided.					
Agitation:	Recommended. Intensity depends on application.					
pH:	6 to 7					
Temperature	30-70 °C. Optimum around 60 °C.					
Specific Gravity	10° Baumé minimum.					
Current Density	Depends on metal content& degree of agitation.					
Current Efficiency:	100 to 112 percent.					



Fig. 1—Hull Cell panels—sulfite gold system at pH 6.5 (0.5 A, 5 min, 60 °C): (a) without additives; (b) with 30 ppm arsenic; (c) with 12.5 mL/L organic brightener.

specular range to about 15 mA/cm<sup>2</sup>. A proprietary organic brightening agent increases the overall reflectivity of the deposit (Fig. 1 c) and provides leveling, such that the deposit brightness increases with increasing thickness, at least up to about 20  $\mu$ m. The plating solution is operable in conjunction with various other brightening and alloying additives.

Without a prior strike, adhesion of the gold deposit to copperbased alloys and to electroless nickel is generally good. Adhesion to electrolytic nickel is generally satisfactory at solution temperatures above about 50°C, but has been marginal at lower temperatures. A Woods' nickel strike is recommended for plating over electrolytic nickel. A sulfite gold strike based on the present system is under development.

### Physical Properties of Deposit

Without brightening agents, the hardness of gold deposits from the present system is in the range of 60 to 70 Knoop (all microhardness indentations in this study were made at 25g load). Addition of 30 ppm arsenic to the plating solution does not increase the deposit hardness. This is contrary to experience with the pH 9.5 system, wherein such a concentration of arsenic increases hardness to about 130 Knoop. Addition of the organic brightener at about 12.5 mL/L increases the deposit hardness to about 160 Knoop, and changes the crystal orientation from (100) to (111) as well.

Figure 2a shows a surface micrograph of an unbrightened deposit plated from the present system to a thickness of about three  $\mu$ m. The grain clusters are well-defined and highly uniform. Figure 2b, at the same magnification, shows the surface topography of an unbrightened gold deposit plated to three  $\mu$ m thickness from a neutral cyanide system. The grain clusters are significantly larger and less uniform in size distribution than those from the sulfite system. Figure 2c shows the surface topography of a deposit plated from the sulfite system to 30  $\mu$ m thickness. This micrograph shows the development of hillock-like surface features and an increase in size of the grain clusters are about the same size, but of greater uniformity than those from the neutral cyanide system at three  $\mu$ m thickness.

For deposits plated at 1 to 2 mA/cm<sup>2</sup> from the sulfite gold solution without brightening agents at 50 to 60 °C, internal stress has been measured as  $10^{\circ}$ to  $10^{\circ}$ dynes/cm<sup>2</sup>(1 .45 to 14.5 x 103 psi) compressive.

X-ray diffraction data for deposits from the sulfite gold system were determined, as in previous work,<sup>6</sup>by plating gold-struck brass panels in a Hull cell at 0.5 A for five min under various conditions, and scanning the resultant panels with a goniometer at various values of the indicated current density. Data thus obtained are shown in Table 2, together with some reference data reprinted from previous work. For each data set in Table 2, the first column shows relative intensities for the various crystal planes obtained using a randomly oriented powder sample as published by ASTM.<sup>7</sup>All data are normalized to the signal intensity of the (111) crystal plane.

Without additives, deposits plated by DC from the present solution are strongly (100) oriented at current densities up to 6 mA/cm<sup>2</sup>. Pulse plating with 0.25 msec pulses at 50 percent duty cycle increases the degree of (100) preference still further. Deposit hardness measured under both these conditions is in the range of 60 to 70 Knoop. Addition of 30 ppm arsenic to the plating solution has relatively little effect on deposit brightness or crystal orientation at current densities up to 2 mA/cm<sup>2</sup>. Above 4 mA/cm<sup>2</sup>, however, deposit brightness is increased, and the crystal orientation approaches (111). Deposit hardness in the brightened condition remains in the range of 60 to 75 Knoop. This is in contrast to the pH 9.5 system, in which addition of 30 ppm arsenic produces a hard (120 to 140 Knoop) deposit which is highly (110) oriented and bright only up to about 4 mNcm<sup>2</sup>.

Addition of a proprietary organic brightening agent to the pH 6.5 solution yields a hard (160 to 170 Knoop) bright deposit which is strongly (111) oriented. The (111) is the most densely packed crystal plane in gold, and deposits oriented with the (111) plane parallel to the surface offer generally superior resistance to abrasive wear. The organically brightened de-

# Table 2X-Ray Diffraction Data

			Curren	t Density,	mA/cm <sup>2</sup>			
Randon	n (hkl)	2	4	6	10	15		
Sulfite. pH 6.5. no additions. D. C., 60 °C								
100.0	(111)	100.0	100.0	100.0	100.0	100.0		
46.0	(200)	102.7	153.9	200.2	74.9	36.3		
32.0	(220)	0.5	0.3	0.7	1.8	5.8		
33.0	(31	1) 3.6	3.5	4.1	6.7	13.4		
Sulfite. pH 6.5. noadditons. pulsed 0.25 msec "on" 0.25 msec "off". 60°C								
100.0	(111)	100.0	100.0	100.0	100.0	100.0		
46.0	(200)	235.5	429.3	264.9	85.7	30.8		
32.0	(220)	0.5	0.4	0.5	1.4	5.3		
33.0	(311)	2.4	3.3	3.3	6.9	10.7		
Sulfite, pH 6.5.30 ppm arsenic, D. C., 60 "C								
100.0	(111)	100.0	100.0	100.0	100.0	100.0		
46.0	(200)	155.6	53.2	29.6	15.7	21.7		
32.0	(220)	1.0	6.0	16.9	0.3	2.4		
33.0	(31	1) 3.0	6.3	16.5	2.5	13.5		
Sulfite. pH 6.5, 12.5 mL/L organic, D. C., 60 °C								
100.0	(111)	100.0	100.0	100.0	100.0	100.0		
46.0	(200)	16.5	14.7	14.7	15.4	14.5		
32.0	(220)	18.6	19.7	22.8	23.6	24.8		
33.0	(311)	14.5	18.7	17.7	17.1	19.3		
Neutral cvanide, pH 5.7, no additions, D.C., 60 °C								
100.0	(111)	100.0	100.0	-,	100.0			
46.0	(200)	31.3	38.6		21.8			
32.0	(220)	5.0	4.9		10.8			
33.0	(311)	14.5	14.2		32.2			
Acid cyanide, pH 4.2, 2000 ppm cobalt, D. C., 33 'C								
100.0	(111)	100.0	100.0		100.0			
46.0	(200)	30.5	29.1		14.8			
32.0	(220)	11.7	7.3		3.7			
33.0	(311)	11.6	14.5		6.3			
Sulfite, pH 9.5,30 ppm arsenic, D. C., 50 "C								
100.0	(111)	100.0	100.0					
46.0	(200)	90.0	66.7					
32.0	(220)	472.0	219.0					
33.0	(311)	171.0	70.0					

posit from this system appears to have properties substantially identical to those of the so-called hard acid golds, which are cyanide-based solutions of pH about 3.5 to 5, using cobalt, nickel, or iron as brightening agents.

In previous work,<sup>618</sup> we showed that the position and slope of porosity vs. thickness curves for various gold deposits were influenced by the deposit grain size and the crystal orientation. Porosity vs. thickness plots for deposits from the present sulfite system have been generated, and are shown in Fig. 3. Specimens for this series of measurements were generated by barrel plating procedures, the details of which have been described previously. <sup>6</sup>Porosities were determined by corrosion potential measurements in 0.1 M NH<sub>4</sub>Cl.<sup>9</sup>

In corrosion potential testing, the plated specimen is immersed in an electrolyte which is a mild, non-filming corrodant for the base metal, but inert to the coating. The potential of the plated specimen vs. a reference electrode in such an electrolyte is proportional to the logarithm of the exposed area or area fraction of base metal. The substrates for this series of determinations consisted of small copper electrical terminals.<sup>10</sup>

The plots in Fig. **3** were generated from specimens plated in the pH 6.5 sulfite system (A) without additives, (B) with 30 ppm arsenic, and (C) with 12.5 mL/Lof the organic brightener. Curve (D) in Fig. 3 is data from the pH 9.5 sulfite system with 30 ppm arsenic, and has been reported previously.

In general, the data shown in Fig. 3 are consistent with previous results.<sup>68</sup> The plots shown are multisegmented. In previous studies, we had postulated that at low deposit thicknesses, the growth of the electrodeposit is largely influenced by the characteristics of the substrate, whereas at higher thicknesses the porosity-thickness curve becomes characteristic of the electrodeposit itself. Between these two regimes, there is a transition region in which the apparent porosity decreases rapidly. The nature of the electrode processes occurring in the



Fig. 2—Deposit surface topography: (a) pH 6.5 sulfite gold, no additives, thickness 3  $\mu$ m; (b) pH 5.7 cyanide gold, no additives, thickness 3  $\mu$ m; (c) pH 6.5 sulfite gold, no additives, thickness 30  $\mu$ m. 5000X.



Fig. 3—Porosity vs. thickness—sulfite golds: (A) pH 6.5, no additives; (B) pH 6.5, 30 ppm arsenic; (C) pH 6.5, 12.5 mL/L organic brightener; (D) pH 9.5, 30 ppm arsenic.

transition region has never been specified. It maybe observed, however, that for the system gold-copper in 0.1 M NH,Cl, the transition always begins at copper area fractions between  $10^4$  and  $10^5$ . At this point it appears that this may represent a transition In the cathode reaction kinetics from diffusion to activation control.

Gilmer has shown that for a perfect single crystal of a facecentered cubic material the rates of growth of the (111), (100) and (110) faces are in the order 3:4:5.<sup>11</sup> Consequently, the slopes of porosity-thickness plots for (111)-, (100)- and (110)oriented deposits should increase in approximately this ratio. Similarly, because the density of atomic packing is greatest in the (111) plane, followed by the (100) and (1 10) planes, the covering power of the various deposits should be in the order (111) > (100) > (110).

The plots shown in Fig. 3 conform to the order predicted. The unbrightened deposit(A), which is (100)-oriented, shows poorer covering power, but much more rapid slopes than the organic-brightened deposit (C), which is (111)-oriented. The arsenic-brightened deposit (B) shows a plot roughly parallel to that of the unbrightened deposit. The plating runs used to generate



Fig. 4—Porosity vs. thickness, (111)-Oriented Golds: (C) pH 6.5 sulfite, 12.5 mL/L organic brightener: (E) pH 5.8 cyanide, no additives; (F) pH 4.2 cyanide, 2000 ppm cobalt.

these samples were performed at approximately 1 mA/cm<sup>2</sup>. From the diffraction data, arsenic does not significantly affect deposit orientation below about 2 mA/cm<sup>2</sup>, so that the two plots would be expected to be roughly coincident. The degree of separation of the plots seen here probably results from inconsistency in preparation of the substrates, and is indicative of the magnitude of the experimental error. Curve (D) of Fig. 3 was obtained using a pH 9.5 sulfite gold with 30 ppm arsenic. The deposit is hard (120-130 Knoop) and (110)-oriented. The slope of Curve (D) is roughly parallel to that of the lower portion of Curve (A).

Figure 4 shows porosity-thickness plots of a series of gold deposits, **all** of which nucleate with (111) preferred orientation. Curve (E) represents a neutral cyanide gold system without additives. The lowermost portion of this plot is very shallow, which is attributed to growth of the grain clusters with increasing deposit thickness, as shown in Fig. 2b. Deposits of this type have been shown to nucleate with strong (111)-preferred orientation, but to roughen and become randomly oriented as

deposit thickness is increased.<sup>12</sup>Curve (F) is representative of a cobalt-brightened hard acid gold. Deposits of this type are known to preserve a strong (111) orientation, as well as grain sizes of the order of 3 X 10-8 cm to thicknesses of 5 µm and greater.

The lowermost portion of Curve (F) is considerably steeper than that of Curve (E), which indicates that even among (111)oriented deposits, the rate of pore closure is greatest for deposits of finest grain size. From Fig, 4, one would expect the grain size of Deposit (C) to be somewhat larger than that of Deposit (F), even though the degree of (111) preference is approximately equal for both. It was mentioned previously that Deposit (C) exhibits leveling properties, as does deposit (D). This does not appear to affect the porosity-thickness plots, presumably because the effect becomes noticeable over thicknesses greater than those reported here.

Finally, it is understood that electrodeposits are microcrystalline, and only very rarely of single orientation. If, however, the plots of Deposits (F), (A) and (D) are compared as representative of strongly preferred (111), (100) and (1 10) orientations, it maybe observed that the slopes are approximately in the order 3:4:5.

#### Summary

A stabilized sulfite gold plating system is capable of controlled operation at pH values as low as 4.0. Its operating characteristics have been described, when maintained in the range of pH 6 to 7, as well as some physical properties of deposits obtained from it under a variety of conditions.

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