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Gold Plating Using the Disulfiteaurate Complex

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ABSTRACT

To improve the stability of a gold sulfite plating bath, decomposition behavior and evaluation of stabilizing agents was investigated. Stability can be improved by the inhibition of the disproportionation reaction. The most effective stabilizing agents were 2,2'-dipyridine and its derivatives. Addition of 2,2'-dipyridine did not influence the hardness of the deposit, and the stress of the deposited film was significantly decreased.

Soft gold plating is used in the electronics industry, especially for semiconductor devices. Most soft gold baths are based on KAu(CN)₂, KH₂PO₄, potassium citrate, and trace amounts of an additive.¹ However, cyanide-containing electrolytes tend to penetrate the organic photoresist which is applied to fabricate metal bumps or conductive circuit patterning. Penetrated residues under the resist cause insulating problems. In comparison, gold sulfite plating processes²⁻⁴ are not sensitive to the resist. However, this bath gradually degrades after passing current, and a black colloid is precipitated in the bath. In this paper, we report on an improvement to gold sulfite bath stability.

Experimental Methods

A basic bath composition and operating conditions are shown in Table I. A test piece consisted of a 2 μ m thick nickel-plated copper

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Table I. Bath composition and plating conditions.

Na ₃ Au(SO ₃) ₂	0.06 (<i>M</i>)
Na ₂ SO ₃	0.60 (<i>M</i>)
H ₃ PO ₃	0.30 (<i>M</i>)
μĂα	8
Temperature	60°C
Current density	0.5 A/dm ²
Load factor	0.5 dm ² /liter
Agitation	Mechanical agitation

Preplating: Watts Ni 3 µm. Counterelectrode: Ti-Pt mesh.

Table II. Bath stability with quantities of electricity.

Stabilizer	Quantity of electricity (C)
Standard bath	30
1,5-Naphthalenedisulfonic acid (1 g/liter)	30
Benzenesulfonic acid (1 g/liter)	33
m-Aminobenzenesulfonic acid (1 g/liter)	55
Pyridine (100 ppm)	40
2,2'-Dipyridine (1 ppm)	60
2,2'-Dipyridine (100 ppm)	400
2,2'-Dipyridine (100 ppm)	900
o-phenanthroline (200 ppm)	300
Neocuproin (200 ppm)	260
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sheet, pretreated with an alkaline degrease and activated with sulfuric acid before use. The quantities of electricity passed were measured by a coulometer prior to decomposition of the bath. The loss of bath stability was confirmed by a color change and decomposition of the solution. Changes in complexes in the plating solution were measured with a UV-visible spectrophotometer (Shimazu MPS-2000). Deposited gold hardness was measured by the Vickers microhardness tester with a 1 g load. The stress was measured by a deposit stress analyzer (Model 683EC Electrochemical Company, Incorporated). Surface morphology was observed by scanning electron microscopy (SEM).

Results and Discussion

Gold sulfite plating solution is colorless and transparent. Generally metallic and black-colored colloids gradually precipitate as plat-



Fig. 1. Absorption spectrum curves for decomposing gold sulfite complex solution. 1, Standard; 2, 50C, 3, 100C; 4, 400C, 5, HAuCl₄ (as Au; 80 ppm); and 6, 2,2'-dipyridine (100 ppm), 900C.



Fig. 2. SEM micrographs of Au bump from cyanide bath and gold sulfite bath. (a) Patterns of photoresist, (b) bump from cyanide bath, (c) bump from sulfite bath.

ing proceeds and finally the bath is decomposed. Black colloidal precipitate is produced after only 30 C of charge have passed. The following mechanisms for the decomposition phenomenon of the bath can be postulated: (i) reduction of gold ions by sulfite ions, (*ii*) reduction of gold ions by phosphorous ions, (*iii*) anodic oxidation of sulfite ions, and (*iv*) disproportionation reaction of gold (I) ions.

Sulfite ions and phosphorous ions were quantitatively determined by an isotacophoretic analyzer. Sulfate ion concentration was not changed during the plating and also the oxidation reaction of phosphorous to phosphoric ions was not observed. Therefore, phosphorous and sulfite ions were not involved in the decomposition or the reducing reaction of gold (I) ions. To determine the decomposition reaction, the plating bath was divided into cathode and anode chambers by an ion-exchange membrane and both chambers were observed. The decomposition reaction by colloidal precipitation was found only in the cathode chamber. Therefore, only reduction of gold (I) ions seems to be involved in the decomposition reaction. A color change from colorless to purple was also found before decomposition of the solution. To investigate the color change, UV spectra were measured. The result is shown in Fig. 1. Only an absorption based on a sulfate ion was found in a fresh bath. A new absorption peak appeared at 313 nm after passing charge, and the peak gradually increased with increasing charge passed, and finally a black colloidal precipitate was formed. The absorption peak seems to have originated from a change in the gold complex ions. Spectroscopic analysis of various kinds of gold salts was performed. An absorption peak at 313 nm was detected in a diluted sodium tetrachloroaurate solution containing gold (III) ions.⁵ Therefore, the absorption peak that appears at the onset of decomposition of the bath is based on the existence of gold (III) ions. Discharge of the gold sulfite complex consists of the following three steps

 $Na_{3}Au(SO_{3})_{2} \rightarrow 3Na^{+} + Au(SO_{3})_{2}^{3-}$ [1]

$$Au(SO_3)_2^{3-} \rightarrow AuSO_3^- + SO_3^{2-}$$
[2]

$$AuSO_3^- + e \rightarrow Au + SO_3^{2-}$$
[3]

The charge transfer of Eq. 3 is the rate-determining step. Accordingly, free gold (I) ions accumulate at the reaction interface and cause a disproportionation reaction according to Eq. 4

$$3Au^+ \rightarrow 2Au + Au^{3+}$$
 [4]

Metallic gold and gold (III) ions are formed in the solution which becomes turbid by colloidal precipitation and finally decomposes. Therefore, the bath stability can be improved by the retardation of the disproportionation reaction. Various kinds of organic compounds that can form complexes with gold (I) ions were added to the standard bath in order to improve the bath stability. The results are shown in Table II. The standard bath decomposed after passing 30 C of charge. In contrast, a remarkable improvement was achieved by the addition of 2,2'-dipyridine to the bath. The absorption peak based on Au(III) ions at 313 nm increased as plating proceeded for the standard bath, however, this peak did not appear and no black colloidal precipitate was formed, even after passing 900 C in the presence of a 2,2'-dipyridine addition. These results are also shown in Fig. 1 where 2,2'-dipyridine and its derivatives cause a retardation effect on the decomposition reaction. It is believed that the effect is due to the presence of unshared electron pairs associated the 2,2'-dipyridine and derivatives that allows the formation of complex ions with gold(I) ions at the discharge interface and hence increase the bath stability. The surface morphologies of the plating films from the standard bath and the bath containing 2,2'-dipyridine both show a dull appearance. However, the grain clusters obtained from the 2,2'-dipyridine bath were smaller $(0.3-0.5 \ \mu m)$ than from the standard bath (1-2 $\ \mu m$). The addition of a trace amount of lead, thallium, or arsenic⁶⁻⁹ to cyanide-based soft gold plating baths is a common means of brightening. A bright film was obtained from the gold sulfite plating solution by an addition of arsenic. Other additives did not improve the brightness. No significant difference of hardness was observed between the 2,2'dipyridine-containing bath and the standard bath. The Vickers hardness was approximately 66 Hv. However, the hardness was increased to about 100 Hv by the addition of arsenic. A significant change in hardness was not observed after the heat-treatment of these films. The stress in the film from the standard bath was

compressive with a value of approximately 2.50 kg/mm². This was substantially decreased to 0.86 kg/mm² by the addition of 2,2'-dipyridine. However, the stress was increased to 6.52 kg/mm² by the addition of both 2,2'-dipyridine and arsenic. From the x-ray diffraction analysis of the plated films, the deposited crystal orientation was not changed by the addition of 2,2'-dipyridine. However, the (111) texture was strongly promoted by the addition of arsenic. The gold sulfite bath containing 2,2'-dipyridine has been applied to the fabrication of a gold bump. Figure 2 shows SEM photographs of gold-plated bumps from both cyanide bath and sulfite bath before (Fig. 2a) and after elimination of the photoresist. Cyanide electrolyte penetrated the photoresist and produce a deformed bump (Fig. 2b). The gold sulfite electrolyte did not attack the resist and produced a clear straight-sided bump (Fig. 2c).

Summary and Conclusion

The decomposition mechanisms and evaluation of stabilizing agents were investigated for a gold sulfite plating electrolyte. It is confirmed that Au metal and Au^{3+} ions were produced in the plating solution during the decomposition reaction. Decomposition of the gold sulfite plating bath was due to a disproportionation reaction as follows

$$3Au^+ \rightarrow 2Au + Au^{3+}$$

Stability can be improved by the addition of 2,2'-dipyridine and its derivatives. These agents inhibit the disproportionation of Au^+ and greatly improved the bath stability. The Vickers hardness of the deposit from the bath containing 2,2'-dipyridine had a value of 66 Hv, and the stress was lower than the standard bath. Brightness was improved by the addition of arsenic, but this increased the hardness and the internal stress.

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