A Thiosulfate-Sulfite Gold Electroplating Process for Monolithic Microwave Integrated Circuits (MMICs)

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The application of gold-plated MMIC substrates such as GaAs and InP in military, aerospace and satellite communication systems is well established. After the initial thin film of Cr/Au or Ti/Au deposition by evaporation/sputtering, the substrates are gold plated from a bath containing KAuCN₂/NaAuCN₂. Besides being pollutants, these baths are deterimental to positive photoresists employed for delineating conductive patterns. Non-cyanide alternatives containing sulfite and thiosulfate-sulfite have been practically successful. The currently available baths operate at 60° C (140° F) in the pH range of 9.0-6.0. A bath was developed that works at 25-30°C (77-86° F) and a pH of 4.6 - 4.8. These operating conditions are compatible with various electronic components. Bath parameters and coating properties are compared with those of conventional CN bath.

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The use of MMICs based on semiconducting $Na_3Au(S_2O_3)_2$. substrates such as GaAs and InP in aerospace densities and molar ratios of and satellite communication equipments is wellknown. Metallisation is an important step in the fabrication of passive components such as resistors, inductors, capacitors, air bridges and transmission lines¹. Gold is the most preferred metal owing to its high electrical conductivity, environmental stability and low attenuation at microwave frequencies. However, its poor adhesion necessitates deposition of an intermediate layer of Cr(200A°) /Au(1000A°) or Ti(200A°)/Au(1000A°) by evaporation/sputtering prior to final electroplating upto 3-5µm (120 - 200μ in) on the above substrates.

Pure gold (99.99%) known as "soft gold" is traditionally plated from a neutral (pH :7-8) or acidic (pH :4-6) cyanide bath at 60°C (140°F). These baths are strong pollutants due to formation of CN⁻ ions during electrodeposition². Hence, alternative baths based on gold halides, thiocyanate, thiourea, ammonia, sulfite and thiosulfate-sulfite complexes have been investigated. Of these, only the last two baths are widely reported in the literature³⁻⁶.

The sulfite baths plate gold at 60°C (140°F) in the pH range of 8-9. Further, with additives their bath pH values were decreased upto 6.5-4.0. However, it was found that below pH : 5.0 rapid⁷. evolution of SO₂ becomes The thiosulfate-sulfite bath also operates at 60°C (140°F) and pH : 6.0. Hence, the objectives of present study were i). To investigate а thiosulfate-sulfite bath working at 25-30°C (77-86°F) and pH : 4.6 - 4.8, so that any electronic component may be plated with minimum damage ii) to compare the bath parameters and properties of gold coating from this bath with that of a CN bath iii) to electroplate gold on Cr/Au coated GaAs substrate and iv) to throw some light on the mechanism of gold electrodeposition from the above bath.

Experimental Procedure

Bath Optimisation

Reagent grade chemicals and DI water were employed in bath preparation. The gold salt used sodium aurothiosulfate, was

2H₂O. Optimum current



[Na₃Au(S₂O₃)₂]:[Na₂SO₃]were found out from Hull cell studies.

Several strike baths containing Au (1g/L) (0.13 oz./gal.) as thiosulfate and different ratios viz, 1:1, 1:2, 1:3 of the above salts adjusted to pH 4.6 -4.8 at 25-30°C (77-86° F) were taken in Hull cell. The cathode panels consisted of Ni plated Cu (Ni/Cu) substrates, previously cleaned/ etched and a platinised Ti mesh was used as anode. The panels were plated at very low cell currents in the range of 0.05-0.20A for 1 min. and inspected for brightness, uniformity and the covering power.

Next, strike Au plated panels were further gold plated for 5 min. in the main bath containing 8g.Au/L(1oz/gal.) and other constituents under similar conditions. Only the typical panels are shown in Fig.1.

Comparative Studies with CN Bath

The bath characteristics and properties of gold coating from the optimised thiosulfate-sulfite bath compared were with those of а conventional acidic cyanide bath of the following specification: KAuCN₂ : 8g.Au/L (1 oz./gal.), K₃ citrate: 50 g/L (6.7 oz./gal), citric acid : 20 g/L

(2.7 oz/gal.) till p (140°F), C.C.D.:(H : 4.5, I 0.5A/dm ²	bath temp.: 60°C (4.6A/ft ²) and	Scotch tape/ heat quench at 250°C (482°F) for I hr. as per ASTM specification ⁸ .	
			Sheet Resistance	
The throwing power measurements were made in a Haring-Blum cell with Pt - Ti anode and two strike Au plated Ni/Cu substrates kept on either side of anode at distances of 2.5 cm (I in) and 12.5 cm (5 in). Electroplating was performed for 30 min. each for thiosulfate-sulfite and CN baths.			For these measurements gold was electroplated to $5\mu m$ (200 μin) thickness on electroless Ni plated Al ₂ O ₃ (Ni/Al ₂ O ₃) substrates. The sheet resistance was measured with a Four Point Probe meter. <i>Surface Morphology</i>	
For cathode current efficiency (C.C.E.), Pt coupons 25 x 25 mm, 0.1 mm thick (1 x I in, 0.004 in thick) were employed. After cleaning/etching, gold was electroplated by passing 100 coulombs through a digital ampsec. meter. Efficiency was estimated from difference in weights before and after plating (W_{expt}) and using the standard formula, C.C.E. = $W_{expt}/W_{theor} x 100$.			5μm (200μin) thick gold was deposited on 10 x 10 mm, 0.6mm thick (0.4 x 0.4 in,0.025 in thick) Ni/Al ₂ O ₃ substrates and the surfaces were examined by Scanning Electron Microscopy (SEM). The images are shown in Fig. 2. <i>Gold Plating of GaAs Substrate</i> The thiosulfate-sulfite bath developed above was tested for gold electroplating of a semi insulating (SI) GaAs wafer. A 500µm thick wafer was given a meticulous pretreatment consisting of cleaning, native oxide etching with NH ₄ OH $+H_2O_2 +H_2O$ mixture, ultrasonic degreasing and Cr/Au evaporation prior to final gold electroplating to 5µm. (100µin) thickness. The process flow chart is given in Fig.3.	
Analysis of Gold Coating				
Gold deposited on Pt coupon was dissolved in aqua regia, diluted with distilled water and analysed for trace impurities by ICP method.				
Purity of gold was checked on a X-ray spectrometer at 60 kV and 50 mA. These values are listed in Table 1.				
Thickness				
Thickness of gold coating was tested by both weight difference and Beta Backscatter method.				
Analysis of	Gold Coating Thiosulfate- Sulfite bath	s Cyanide bath		
Assay (Au%) Impurities(ppm) Cu Ag, P, S, K, Na,Fe,Cd, Zn	99.99	100.0	a	
	6.7	1.7	20.000 PR 20.0kU 2000	
	< 0.1	< 0.1	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	
Grain Size				
The mean grain sizes of gold coatings were found by using an Image Analyser			Fig. 2: SEM images of (a) thiosulphate - sulphite (b) cyanide produced gold deposits on Ni/ Al ₂ O ₃ substrates	
Coating Adhesion				
Adhesivity of gold electroplated on substrates with Ni under coats as well as Cr/Au plated GaAs wafer was checked qualitatively by a				



Fig. 3: Process steps for gold electroplating

on GaAs substrates

Results and Discussion

The electrodeposition of gold from a thiosulfatesulfite bath may be assumed to take place stepwise as follows :

 $Na_3Au(S_2O_3)_2 \rightarrow 3Na^+ + [Au(S_2O_3)_2]^{-3} ...(1)$ $[Au(S_2O_3)_2]^{-3} \rightarrow [AuS_2O_3]^{-1} + S_2O_3^{-2} \dots \dots (2)$ $[AuS_2O_3]^- + e \rightarrow Au + S_2O_3^{-2}$... (3)

bath is not stable due to instability of The thiosulfate ion forming sulfur according to reaction :

 $S_2O_3^{-2} \leftrightarrow S + SO_3^{-2}$

The forward reaction in eqn. 4 can be suppressed by adding SO_3^{-2} ions to the bath.

The molar concentration of Na₂SO₃ to be added can be found out from inspection of Hull cell samples. It was revealed that the optimum ratio of $[Na_3Au(S_2O_3)_2]$: $[Na_2SO_3] = 1 : 1$. This points out to the possibility of formation of a mixed complex of the formula $[Au(S_2O_3)_2 (SO_3)]^{-5}$ as follows :

$$Au^{+}+2S_{2}O_{3}^{-2}+SO_{3}^{-2}\rightarrow [Au(S_{2}O_{3})_{2}(SO_{3})]^{-5}...$$
 (5)

The stability constant of the above complex is not known. However, it must be more than that of Na₃Au(S₂O₃)₂ i.e. $,10^{26}$.

It is interesting to note from Table 2 that the cathode current efficiency of thiosulfate-sulfite bath is 95 - 120%, much higher than that of CN bath. It implies that the current employed is fully utilized for gold deposition with negligible gas evolution at the cathode. Hence, the cathode solution interface needs mechanically induced i) A thiosulfate-sulfite bath for electroplating agitation by cathode movement. Besides, a 100% throwing power ensures uniform gold

coating even in recessed areas of substrates. These properties along with very low cathode

Table 2 Thiosulfate -Sulfite vs Cyanide bath					
Parameter/ Coating property	Thiosulfate Sulfite bath	Cyanide bath			
Bath pH Bath Temp	4.64.8 25-30°C (77-86°E)	4- 6 60°C (140°E)			
C.C.D. C.C.E.	(77-86 F) 0.03-0.3A/dm ² (0.3-3A/ft ²) 95 - 120 %	(140 F) 0.5-2A/dm ² (4.5-18A/ft ²) 57 - 90 %			
Throwing power Coating adhesion Mean grain size Sheet resistance	100% Fair 1.53μ m (61 μin) 2.1μ Ω cm	65-75 % Good 1.99μ m (80μ in) 2.0μ Ω cm			

current densities required for electrodeposition as well as inferior coating adhesion are characteristics of an electroless plating bath. In fact, some investigators have found that the Au(I)thiosulfate-sulfite mixed ligand system functions as an autocatalytic bath without any additional reducing agent⁹.

However, electroless plating was not observed on Cr/Au coated GaAs wafer due to a noncatalytic property of Cr underlayer.

A comparison of SEM images in Fig.2. shows a closely packed uniform grain structure for thiosulfate-sulfite and a spherical crystalline structure for cyanide gold deposits. It is known that fine grained deposits are required for fabrication of semiconductors.

Since the sheet resistance values of gold coatings from both baths are identical, the thiosulfate-sulfite bath may be preferred due to its eco-friendly nature. It is well known that higher the electrical conductivity of coating, lower is microwave attenuation/insertion loss, which is a prerequisite for metallisation of MMICs.

Conclusions

gold at 25-30°C (77-86°F) and pH:4.6-4.8 has

been studied. It contains $Na_3Au(S_2O_3)_2$ and Na_2SO_3 in a molar ratio of 1 : 1.

ii) This bath can electrodeposit gold on Cr/Au coated GaAs substrates.

iii A mechanism postulating the formation of a mixed complex of the formula $[Au(S_2O_3)_2SO_3]^{-5}$ has been proposed for electrodepostion.

iv Extremely low cathode current density values, inferior coating adhesion and a 100% throwing power of thiosulfate-sulfite bath indicate an electroless plating property of the bath on Ni plated substrates. However, electroless plating did not occur on Cr/Au coated GaAs substrates.

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