A New High Speed Acid Gold Process, Developed And Characterised for Connector Market

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This paper will describe a new high speed cobalt hardened bright acid gold.

Correlation between the physical properties of the deposition and the composition were observed. The evaluation was undertaken at a range of high current densities and the increases obtained reported. Different techniques of analysis such as Glow Discharge Mass Spectrometry were used and will be explained in this paper.

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Introduction

In spite of a poor 2001 year in electronic industry, the plating of connectors is still very important in miniaturisation of electronic volume The components and the increase of data transmission rates demands an improvement of final gold layer properties of such products. A new electrolyte specially designed for high-speed deposition and low contact resistance has been developed. After a brief reminder of 2001 connector market and what the major players want, we will compare the properties of two types of gold deposits and their composition using Glow Discharge Mass Spectrometry (GDMS) and Glow Discharge Optical Emission Spectrometry (GDOES).

Connector market

2001 presented a fall of 26% in connector activity against 2000. This morosely was due to a lack of sales of electronic products and to an overproduction of connectors at the end of 2000. This decline of production was not geographically regular. Actually the biggest decline was in Japan with 37.8 % down followed by north America with 36.1 % down and Europe with 24.1 % down. Asian went down 20 % except China which 12 % because relocation of progressed manufacturing to a more economically attractive place together with a good technology standard. Despite this high production decline, the connector market remains the biggest gold consumer in plating in the form of gold potassium cyanide essentially. In fact, the connector industry represents more or less 150 tonnes of gold used annually. 75% of this quantity is gold salt for connector plating.

So, the connector market remains a big opportunity in the plating business [1].

Request from major companies

Present request from major connector companies is related to two essential aspects: economical issues and technical issues. Economical issues, at the process level is leading to a lower quantity of precious metal tied up, by a lower precious metal concentration in the bath, and by a higher deposition rate allowing a productivity gains. Two attitudes can be adopted: to choose a productivity increase while keeping the same precious metal concentration in the bath, or to keep the same productivity but decrease precious metal tied up. The technical issue at the deposit level, is to achieve a lower contact resistance at lower thickness while keeping intact other deposit properties i.e. good ductility, low porosity, good distribution, good solderability, good wear resistance, high hardness etc.

Characterisation of the new high speed gold process cobalt hardened

A new high-speed acid gold, cobalt hardened, had been developed in order to meet of the previous requirements. A series of deposits were studied with analytical tools, which are an original method in connectors plating, like GDMS and GDOES. This kind of analysis allows us to establish a depth profile concentration of the different elements presents in the deposit. The samples studied (Fig.1., Fig.2.)



Fig.1: SEM photo of 2010 deposit



Fig.2: SEM photo of 2060 deposit

were approximately 4 μ m thick layers of production cobalt hardened gold electroplated on nickel brass coupons from two proprietary baths named here 2010 and 2060^{*}. Both 2010 and 2060 contain citrate buffer, pyridinic brightener, no free cyanide, 12g.L⁻¹ gold potassium cyanide and respectively 1g.L⁻¹ Co and 0.8g.L⁻¹ Co. 2060 contains an additional organic brightener additive. This organic additive increases the cathodic efficiency of the bath. The baths were thus representative of those actually used in manufacturing plants.

The current density and temperature during plating were respectively from 2 to 20 A.dm⁻² (20 to 200 A.ft⁻²) and 55°C (131°F). The anode was titanium platinized and the electrolyte was vigorously stirred (1 m.s⁻¹). Others parameters were adjusted in accordance with each process technical data sheet i.e. gold concentration, cobalt concentration, brightener concentration and pH^{*}.

All samples were investigated by GDOES and GDMS. Sputtering the surface of these samples layer by layer and measuring the emitted beam for GDOES and mass for GDMS of the sputtered material allows a qualitative and quantitative characterisation of the elemental distribution through the depth. All GDOES measurements were performed using a LECO GDS 750A

instrument. All GDMS measurements were performed using a Thermo Elemental VG 9000.

-GDMS and GDOES principle

GDMS and GDOES are well adapted for achieving elemental distribution profiles. Actually, in both techniques argon is introduced in the analysis compartment under low pressure. Plasma is generated by exchange between an anode and the sample which acts as cathode when it is conducting (Fig.3).



Fig.3. GDMS and GDOES source

Under argon bombardment, atoms are extracted from sample surface and thrown up in plasma. In the GDOES technique, excited atoms go back to their constant state and emit a beam with a characteristic wavelength for each atom. The total beam emitted is focused on a wavelength scattering system. In GDMS, atoms extracted are ionised and accelerated to a mass spectrometer which analyses each element as well as its isotopes. The step by step sample erosion during analysis gives a depth profile.

GDOES data requires to know the sputtering rate in masse/time and the emission yield, in accordance with the concept of constant emission yield at constant electrical discharge parameters:

^{*} Please contact L.CHALUMEAU for more details about baths.

$$I_i = C_i * q * e_i$$

 I_i = intensity of the optical emission of each element at the given wavelength.

 C_i =concentration of element i in the sample in masse units

q=sputtering rate in masse/time

 e_i =emission yield

Results and discuss

The characteristics of the processes and the properties of the deposits obtained from them are listed in table 1.

The GDOES and GDMS spectra of gold electrodeposits are shown in figures n°4. All the elements are recorded from a unique sputtering at each layer. GDMS sputtering layer is about 0.7 μ m thick, while GDOES sputtering layer is about 0.1 μ m thick. The thickness on the graphs is expressed in arbitrary unit where the total thickness of the deposit is 1. Thickness 0 corresponds to the deposit's surface and thickness 1 corresponds to the substrate. Some standards of gold deposit were available for GDMS, so it was possible to evaluate quantities of each element in the deposit.

	2010	2060 (New Bath)
[Au] in bath g/L	12	12
Current density	40	80
max	(jet plating)	(jet plating)
Example of	3.6 µm/min @	6.06 µm/min @ 60
deposition speed	20A.dm ²	A.dm ⁻²
in reel to reel		
simulation		
process		
Contact	5 mΩ	3 mΩ
Resistance after		
ageing (1hour @		
250°C)		
Contact	30 mΩ	$< 10 \text{ m}\Omega$
Resistance after		
ageing (1hour @		
250°C)		
Hardness under	160 Hv	180 Hv
20g		
Porosity @ 0.1µm	Non porous	Non porous
Ductility	good	good

Table 1.: Characteristics of 2010 and 2060 process andproperties of deposits

To try to explain carbon compounds included in the deposit only C, N and Co are displayed. N/C, C/Co and N/Co ratios were calculated in order to reveal an eventual correlation between cobalt and cyanide in deposit (Figures n°5-6).

Carbon analysis with GDMS on Fig.4 shows two different behaviours.



Fig.5: C content - GDMS analysis of 2010 and 2060 deposits



Fig.6: C content - GDOES analysis of 2010 and 2060 deposits

At the extreme surface, carbon content is close to 13 atomic ratio $\binom{a}{0}$ for both 2010 and 2060 deposits, and increases abruptly to 16 $\frac{a}{0}$ for the 2060 deposit. It increases slowly to 18 $\frac{a}{0}$ for the 2010 deposit. 2060 carbon content has a quite constant behaviour in bulk of deposit at 15 $\frac{a}{0}$.

GDOES analysis (Fig.6) shows two different behaviours in extreme surface.

They show a high level of carbon content at the extreme surface and plateau. The difference between GDMS and GDOES analysis is that

GDOES shows a gap between 2060 and 2010 carbon content, contrary to GDMS (fig.4).

The slow increase of 2010 is 2% on 4μ m, so may be it is possible to consider the content quite constant also, except on extreme surface where there is a high rate of carbon.

Nitrogen versus depth curves exhibit two different behaviours with GDOES and GDMS. On GDMS (Fig.7) 2010 nitrogen content increases continuously with time sputtering while with GDOES (Fig.8) it increases to reach a plateau with time sputtering.



Fig.7: N content - GDMS analysis of 2010 and 2060 deposits



Fig.8: N content - GDOES analysis of 2010 and 2060 deposits

2060 nitrogen content obtained by GDOES has a similar behaviour to 2010 nitrogen but higher in specific intensity. This is confirmed by GDMS (Fig.7) except that 2060 nitrogen content seems to be constant in the deposit. When GDMS and GDOES curves have different behaviours, the

ratio of the curve's area is calculated and compared for GDMS and GDOES, in order to verify if both methods are comparable on total element content. These ratios are the same in GDMS and GDOES, i.e. $\frac{S_{2060}}{S_{2010}} = 1.4$.

Both GDMS and GDOES figures show constant cobalt content in the deposits with a higher content in 2010 than in 2060 (Fig.9, Fig.10).



Fig.9: Co content - GDMS analysis of 2010 and 2060 deposits



Fig.10: Co content - GDOES analysis of 2010 and 2060 deposits

The low cobalt amount in acid hard gold deposit causes a background enhancement on the GDOES spectrum. However, curve tendencies reveal a linear behaviour.

With the same analytical method, there are two different tendencies at the extreme surface with 2010 and 2060 for both GDMS and GDOES. In fact, 2060 exhibit a decreasing level of cobalt

content and 2010 exhibits an increasing level of cobalt content.

Quantitative analyses by GDMS show that cobalt content is constant and about 0.8 atomic percent for 2060 and 0.9 atomic percent for 2010. Nitrogen content is about 18 atomic percent for 2060 and between 7 and 15 atomic percent for 2010 Carbon content is about 15 atomic percent for both 2010 and 2060 deposit.

 $\frac{[N]}{[C]}$ ratios have the same behaviour as [N] with

 $\frac{[N]}{[C]}$ near 1 for 2060 and increasing from 0.6 to

0.9 for 2010 (Fig.10, Fig.11).

 $\frac{[C]}{[Co]}$ ratios are quite constant and about 18 for 2060 but increase from 15 to 20 for 2010 with sputtering time (Fig.12,Fig.13).

In accordance with $\frac{[N]}{[C]}$ ratios, $\frac{[N]}{[Co]}$ ratios are quite equal to $\frac{[C]}{[Co]}$ ratios for 2060 but increases from 9 (extreme surface) to 17 (bulk) for 2010.



Fig.11: [N]/[C] - GDMS analysis of 2010 and 2060 deposits



Fig.12: [N]/[C] - GDOES analysis of 2010 and 2060 deposits



Fig.13: [C]/[Co] - GDMS analysis of 2010 and 2060 deposits



Fig.14: [C]/[Co] - GDOES analysis of 2010 and 2060 deposits

Comparison between GDMS and GDOES shows a good agreement of analysis except on the extreme surface. High abrasive rate is incompatible with a fine analysis of the extreme surface. Relative carbon and nitrogen concentrations show that in the 2060 deposit all carbon and nitrogen are presumably included in cyanide form. In the 2010 deposit, carbon content is higher than nitrogen content, so all nitrogen in 2010 deposit may be in cyanide form but carbon is partly in cyanide form and partly in aliphatic form. GDMS and GDOES cobalt analyses don't allow us to conclude there is an inclusion of cyanide in the deposits via $Co(CN)_6^{3-}$ or $Co(CN)_5^{3-}$ complexes only as suggested previously [1],[2],[3], but also by another inclusion process. Nevertheless, a high rate of carbon and nitrogen is present in the deposits where $\frac{[C]}{[Co]}$ is higher than 6.

Both 2010 and 2060 bath show some noteworthy differences in their behaviour. although very similar in composition. Two differences allow discerning 2010 and 2060 deposits. The 2060 bath contain 20% less cobalt than 2010 and an additional organic additive, nitrogen free, making up 7% of the total carbon in the bath (pH<5, so very low carbonate contained). High dependence on the ratio between carbon in deposit and cobalt in electrolyte has been previously demonstrated. Indeed, complexing cobalt by EDTA, the carbon quantity in deposit felt significantly [4]. Following this observation, the deposit from the 2060 bath would contain less carbon and less nitrogen than the 2010 deposit. That isn't the case, on the contrary, the 2060 deposit contains more nitrogen than the 2010 and more carbon but less cobalt according to the GDOES and GDMS charts.

So, organic additive favours cyanide inclusion in deposit in addition of the cobalt effect. The organic additive does not add more carbon and nitrogen to the deposit nor oxygen in the 2010 deposit, as the GDOES graph exhibits (Fig.15).



Fig.15: [O] - GDOES analysis of 2010 and 2060 deposits

Many authors have shown that contact resistance was related to cobalt content in acid gold cobalt hardened deposits [5],[6]. This is often verified. This work shows that contact resistance is dependent on bath running parameters. Correlation between cobalt content and contact resistance is changes when values of fixed parameters change and also when the variable parameters change (Fig.16).



Fig.16: Contact Resistance before and after ageing versus cobalt content in 2010. [Au]=8g/L; [Co]=1g/L; $T=55^{\circ}C$; pH=4,7; $5 A.dm^{2} < Current density < 20 A.dm^{2}$



Fig.17: Contact Resistance before and after ageing versus cobalt content in 2060. [Au]=8g/L; [Co]=0.8g/L; T=55°C; pH=4,5; 5 A.dm² < Current density < 20 A.dm²

Fig.16 and Fig.17 exhibit behaviours where contact resistance is independent of the cobalt concentration in the deposit. In the same way, considering carbon content (Fig.18), the 2010 deposit exhibits a large increase of contact resistance versus carbon content while contact resistance of the 2060 deposit is quite constant over a

large range of carbon content in deposit. Carbon content in deposit (ppm)



Fig.18: Contact Resistance versus carbon content in 2010 and 2060

Conclusion

The new bath 2060 presents better contact resistance than old 2010.

Contact resistance is certainly related to extreme surface phenomena. Adsorbed species must be evaluated rather than included species. Further work will be to explore extreme surface by XPS analyses and near surface by slow sputtering GDOES.

Also, contact resistance is not related to cobalt content, but cobalt exists in different forms. So, the relationship between contact resistance and the different forms of cobalt in deposits will be evaluated.

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