A Spectroelectrochemical Study into the Anodic Behaviour of Au in Electrodeposition Baths containing Organic Additives

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Au anodes are commonly used in metal plating processes from cyanide baths. Their use is also of perspective interest for innovative cyanide free systems, in particular for thiourea-based electrolytes being developed [1]. In this paper we propose an electrochemical and spectoelectrochemical study of the anodic behaviour of Au in presence of organic substances which are of interest as complexing and addition agents. It has been recently pointed out that mechanical problems linked to hydrogen incorporation in the electrodeposition of Au and Au-alloys is a major problem for the applications [2]. These problems can be be diminished by use of suitable organic additives [3]. In this study we present data concerning a series of organic additives employed as hydrogen scavengers for perspective use in the plating of Au and Au-alloys from baths containing Au cyanocomplexes or from cyanide-free baths.

A typical cyanide bath adopted for this research has the following composition: Au (as $KAu(CN)_2$) 7.5 g l^{-1}, citric acid 40 g l^{-1}, NH_4-citrate 40 g l^{-1}, pH 6.3.

A typical cyanide-free bath considered in this study is Au(I) (as Au sulphite complex) 50 mM, thiourea 1M, H_2SO_4 0.5 M.

The anodic behaviour is studied by cyclic voltammetry, differential capacitance, electrochemical impedance spectroscopy. Information at a molecular level of the behaviour of the organic additives at the electrochemical interface was obtained by in-situ Raman (Figure 1) and FT-IR spectroscopies (Figure 2).

By this approach interactions can be studied between the nature of the organic addition agent, anodic reactions of additives and dissolution behaviour of Au.
Details of the surface complexes forming during dissolution and co-adsorption behaviour of complexing and additives agents as well as competitive adsorption of additives or passivation effects can be quantitatively addressed.

Fundamental information can be gained to be implemented in the framework of electrochemical engineering considerations related to the stability of the additivation system and replenishment policies.

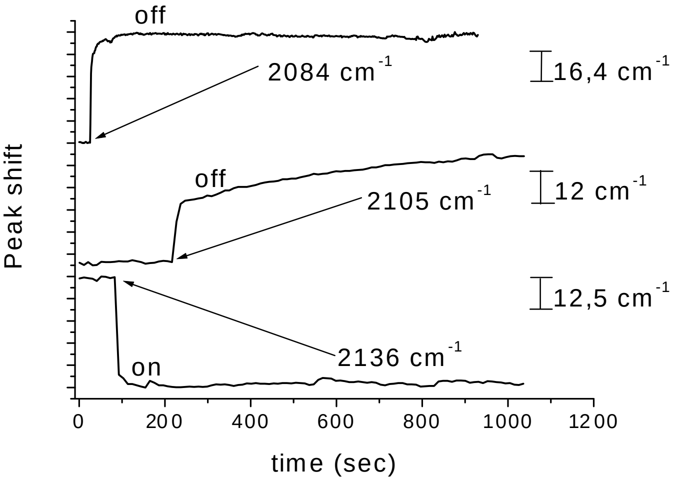

Figure 1 - Peak position transients for the ν_{CN} stretch band from in-situ SERS spectra for potentiostatic experiments in baths without and with BDMPAC: switching "on" and "off" transients.

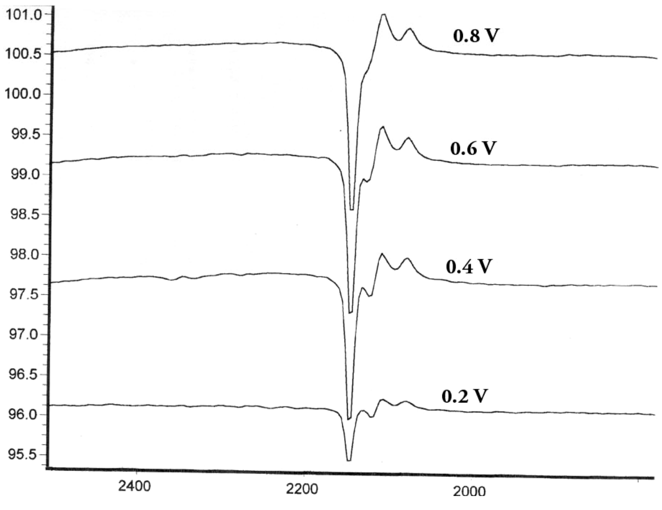

Figure 2 - In-situ FT-IR spectra of the ν(CN) band during in a $KAu(CN)_2$ solution

[1] C.M. Juarez, A.J.B. Dutra. *Minerals Engineering* **10-11** (2000) 1083.

[2] B. Bozzini, G. Giovannelli, S. Natali, B. Brevaglieri, P.L. Cavallotti, G. Signorelli. *Eng. Fail. Anal.* **6** (1999) 83.

[3] B. Bozzini, A. Fanigliulo, M. Serra. *Journal of Crystal Growth* **231** (2001) 589.