

Spectroelectrochemical Studies of Organic Additives for the Electrodeposition of Au

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Mechanical problems and hydrogen incorporation in the electrodeposition of Au and Au-alloys is a major problem for the applications, especially in baths not containing free cyanide and heavy metals [1]. In this study we present an electrochemical and in-situ spectroelectrochemical investigation of the behaviour of a series of organic additives of perspective use for plating of Au and Au-alloys from baths containing Au cyanocomplexes (but no free cyanide) or from completely cyanide-free baths.

In absence of suitable additives, hydrogen typically tends to be incorporated in a low- (~400÷500°C) and in a high-temperature trap (~650÷700°C). Hydrogen incorporation can be reduced efficiently with several additives, selective hydrogen removal from the adsorption traps can also be achieved [2]. Nevertheless side effects can ensue, such as compositional variations of the alloy or incorporation of extraneous material. In particular, some organic addition agents give rise to the appearance of a further, high-temperature peak, which generally contains a large amount of gas. Evidence of organic material incorporation can be achieved also by different approaches [3].

A typical complexed-cyanide bath adopted for this research has the following composition: Au (as $\text{KAu}(\text{CN})_2$) 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 electroodic behaviour was studied by cyclic voltammetry, differential capacitance, electrochemical impedance spectroscopy (Figure 1). Information at a molecular level of the behaviour of the organic additives at the electrochemical growth interface was obtained by in-situ Raman and FT-IR spectroscopies (Figure 2).

By this kind of approach correlations can be recognised between the nature of the organic addition agent on the effect on hydrogen incorporation. Problems related to the co-adsorption behaviour of complexing species and additives as well as competitive adsorption of additives can be quantitatively addressed. Potential dependent adsorption and co-adsorption can be followed and correlated with electrokinetic behaviour as well as structural and morphological characteristics of the deposits electrocrystallised from additive-containing baths.

Cathodic reaction products of additives and the interference of anodic reaction products with the electrocrystallisation process can be assessed.

Figure 1 - Differential capacitance of a Au electrode in $\text{KAu}(\text{CN})_2$ solution

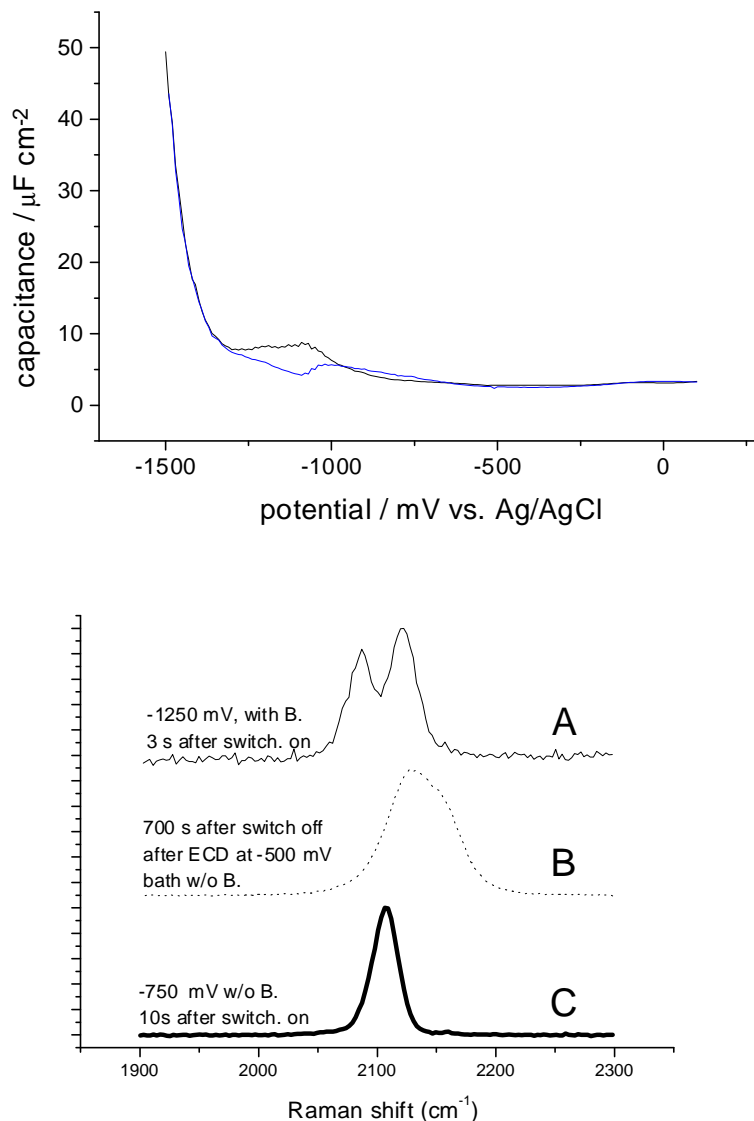


Figure 2 - In-situ Raman spectra of the $\nu(\text{CN})$ band during electrodeposition of Au from a $\text{KAu}(\text{CN})_2$ solution

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

[2] B. Bozzini, P.L. Cavallotti, G. Giovannelli, S. Natali. "Effects of Additives on Hydrogen Incorporation into Au-Cu Electrodeposited from Acidic EDTA Baths" ECS Meeting Abstracts 197th Meeting, Spring 2000, Toronto.

[3] B. Bozzini, A. Fanigliulo. "A Surface Raman Investigation into the Incorporation of Organics into Electrodeposited Au". *Trans. IMF*, in press.