

An Electrochemical Quartz Crystal nano-Balance Study on Cu-Sn Codeposition from Methane Sulphonic Acid Electrolytes

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Introduction

Increasing environmental impact in the past decade has resulted in a concerted search for new electrolytes for electrodeposition. Methane sulphonic acid (MSA) is an interesting supporting electrolyte with many desirable properties such as high salt solubility, high conductivity, low toxicity and corrosivity which enables better waste management [1, 2]. Being an acidic electrolyte it has the added benefit of being compatible with photoresist materials and therefore offers the possibility of being useful for microfabrication. Various researchers have reported on electrodeposition from MSA electrolytes for copper and tin [3, 4] and their alloys [5-11].

Various additives or complexing agents such as brighteners, antioxidants, and surfactants have been shown to be required for Cu-Sn deposition [2, 4, 5-9]. The simplest electrolyte has been shown to require an antioxidant and a fluorosurfactant [5, 6]. The antioxidant, a hydroquinone, is added to stop the spontaneous oxidation of Sn²⁺ to Sn⁴⁺ [4, 6] which would lead to formation of tin sludge.

Although, the fluorosurfactant, DuPont™ Zonyl® FSN, was initially used to reduce hydrogen evolution [9], more recently, it has been shown to prevent the formation of metal oxides [10]. In addition, the inclusion this additive shifts the metal reduction potential of Cu in the cathodic direction, thereby facilitating the co-deposition of the Cu-Sn alloy [6, 11]. In this regard, the role of the fluorosurfactant is crucial and multifunctional, which is not fully understood.

In this work we have further examined the role of fluorosurfactant in shifting the electrochemical reduction potential for the more noble metal. The surface adsorption and desorption processes of the surfactant has been inferred through the use of an electrochemical quartz crystal nanobalance (EQCN). Copper and tin have been deposited individually and simultaneously from methane sulphonic acid electrolytes. Mass changes at the quartz crystal have been compared against those calculated from charge deposited. These data show whether there was adsorption of the fluorosurfactant on the surface of the crystal, and at which potential adsorption/desorption was occurring.

Experimental

Three separate electrolytes were used to deposit Cu, Sn, and Cu-Sn. The copper plating bath was composed of 0.015 M CuSO₄, tin bath contained 0.015 M SnSO₄, and the copper-tin bath contained 0.015 M CuSO₄ and 0.15 M SnSO₄. All electrolytes contained 0.1 M hydroquinone and 2 M methane sulphonic acid. In order to determine the effect of fluorosurfactant, 0.01 %vol fluorosurfactant was added to these electrolytes.

A Seiko EG&G Model QCA917 Quartz Crystal Analyser was used in the experiments. Commercially purchased standard AT-cut, gold coated 9 MHz quartz crystals were used; the active surface area was 0.196 cm². A custom built electrochemical cell, which enabled vertical

positioning of the crystal and has been reported to be stable [12], was used. The voltage change sensed by the quartz crystal analyser was read-off directly by the potentiostat and converted to frequency change. An EcoChemie μ-Autolab II potentiostat with NOVA 1.7 software was used to carry out potential sweeps and record data.

The potentiostat was connected to the QCN with the gold plated quartz crystal acting as the working electrode; the counter electrode was a Pt mesh and the reference was a saturated calomel electrode (SCE). In EQCN experiments cyclic voltammetry was carried out with the forward scan starting from the upper limit of 0.4 or 0.6 V towards the lower limit of -0.6 V and in the reverse scan the potential was increased towards and stopped at the upper limit. The scan rate was 10-50 mV s⁻¹.

Results

It was found that the deposition potential of Sn is not affected by the presence of the surfactant. However, it was found that the adsorption of the surfactant blocks the reduction and oxidation reaction for copper. During the codeposition of Cu-Sn, the surfactant was found to adsorb to the surface and inhibit Cu deposition. However, once the potential reaches a significantly negative value, the co-deposition of Cu-Sn recommences, since the surfactant desorbs.

Conclusions

The result show that not only does the surfactant shift the reduction potential of Cu it also suppresses the reduction current of Cu significantly. Coupled with the fact that hydrogen reduction is stifled, this leads to formation of Sn-rich Cu-Sn films.

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Acknowledgement:

This work was supported by a grant from Newcastle University.

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