

CHARACTERIZATION AND GD-OES INVESTIGATION OF THIN TIN ELECTROPLATED COPPER SUBSTRATES USED IN THE ELECTRONICS INDUSTRY

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Tin electroplated copper sheets were analysed, with the aim of characterizing the structure of the thin film layer deposited on the substrate. The selected raw materials and the plating process are commonly used in the electronics industry for the manufacturing of printed circuit boards. In addition, we used a Hull cell to show the effects of current density distribution on layer deposition. Our research study involved SEM, GD-OES, and optical stereomicroscopic examinations, employed for the structural and qualitative evaluation of layer properties (“layer goodness”). It is clearly visible from the results, that bath composition is not indifferent in the electroplating process: i.e. the distinctive compounds of the bath will be detectable in the outer layers of the coating. Though at high current densities, the coating became spongy, but intermetallic transient phases (e.g. Cu₆Sn₅) were not at all observed at the Cu-Sn interface irrespective of the applied current densities. The grains so formed were mainly equiaxial, with no orientation found.

Keywords: electroplating, tin, copper substrate, Hull cell, GD-OES.

Introduction

Nowadays, a large variety of valuable metals, like tin, copper, silver, nickel, gold, etc. are present in the electronics industry. These metals are all indispensable for the manufacturing of wiring boards, electrical contacts, printed circuits boards (PCBs) and other small electronic components, that are commonly incorporated in consumer goods, e.g. mobile tools, household devices or automobiles. The production technologies largely build on advanced soldering techniques like tin-base lead-free soldering, to connect solid/bulk metal surfaces (Cu, Sn, Ag, Au etc.) or metallized (i.e. metal covered) plates, with high precision. Electroplating is one of the most widely applied metal deposition methods used for creating conductive metal layers on various substrates (i.e. contact pads), e.g. pure

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(lead-free) thin tin layers on pure copper substrates. Of course, there are several other alternatives available for tin deposition, depending on the type of application.

A recent publication on the peculiar features of tin deposition and electrocrystallization from non-alkaline (i.e. acidic) aqueous solutions used in tin recycling processes, especially in tin electrowinning [1], and studies on the spontaneous formation of “tin whiskers” grown on pure, electroplated tin layers [2] impelled us to conduct further investigations on the structural properties of layer deposition. Thus, we performed laboratory experiments on relatively thin electroplated layers of tin deposited onto pure copper sheets, with the aim of characterizing the surface profiles. We used a methanesulfonic acid-base industrial bath obtained from a printed circuit board (PCB) manufacturer (Eurocircuits Co. Ltd. Eger). By using a Hull cell for the electroplating experiments, it was possible to follow, on a single copper cathode sheet, the effect of cathode current density distribution in a relatively wide range. All the other parameters were kept constant during the experiments.

The freshly deposited tin layers were first evaluated via visual observation. Then, several modern testing and surface analytical techniques have been applied, among them Glow Discharge Optical Emission Spectroscopy (GD OES). This method has the capacity to give an in-depth characterization of solid surface layer profiles – including the tin/copper interface and the copper substrate below – in the tens of microns range, within a few minutes measuring time.

2. Laboratory experiments

2.1. Materials and laboratory equipments

The materials used (thin copper sheets, electroplating tin bath) were obtained from the PCB manufacturer company, Eurocircuits Co. Ltd. (Eger), recognized as an online PCB prototype and small series specialist worldwide.

2.1.1. Copper sheet/foils

The thin (~90µm) copper foils (products of IMARO/ELTECH) typically had a shiny side, with an average surface roughness of $R_a \sim 0,2 \mu\text{m}$, and a bonding side with a much higher R_a value. Considering these parameters, only the shiny side (Figure 1) was tin electroplated in the Hull cell, after proper cleaning and degreasing. In order to get the thin (a few nanometers thick) oxide surface layer removed, the foils underwent slight activation via short immersion in an aqueous etching solution of diluted (~ 2%) nitric acid.

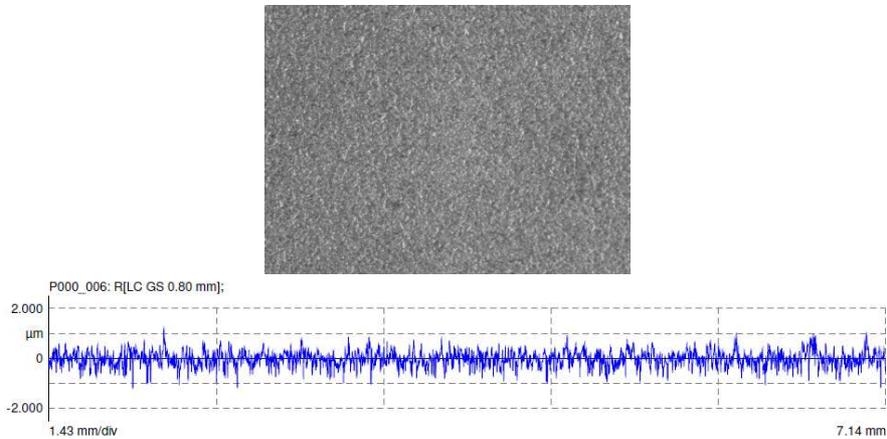


Figure 1. Photograph and profile of the shiny side of the pure copper foils used as substrates for tin electroplating (Magnification = 100 X)

2.1.2. Electroplating bath composition

For the laboratory process, we used a commercial type tin electroplating bath (RESTIN BMAT PC). This fluoroborate-free bath was originally developed for special etch-resist applications in metal etching. Today, an actual technological application of the bath by the producer Eurocircuits Co. Ltd., is SMOBC (Solder Mask Over Bare Copper), that is a preventive method designed to protect the underlying copper sheet while the unprotected thin copper layers of the PCBs are dissolved in an appropriate selective aqueous etching solution. This electroplating bath is highly acidic, due to its free methane-sulfonic-acid content varying between 120 and 200 g/dm³. The bath contains considerable amounts of proprietary additives (so-called Primary and Secondary additives) in order to produce fine grain and smooth dense deposit. Another function of the additives is to protect the dissolved Sn²⁺ ions from oxidation to Sn⁴⁺ as a result of exposure to ambient air during the electrolytic process.

2.1.3. Hull cell used for tin electroplating

The Hull cell is basically a specially shaped container (Figure 2) designed originally for the practical testing of electroplating solutions. The cathode is set at a pre-defined angle to the anode (as shown in Figure 2), to produce an extensive range of current densities. The current densities produced in the Hull cell can be calculated from the geometrical data of the cell, which makes it possible to check and characterize the deposit along the cathode plate as a function of current densities – supposing that the given experiment is performed at a known constant current value (i.e. cell current is applied in the “galvanostatic” operation mode).

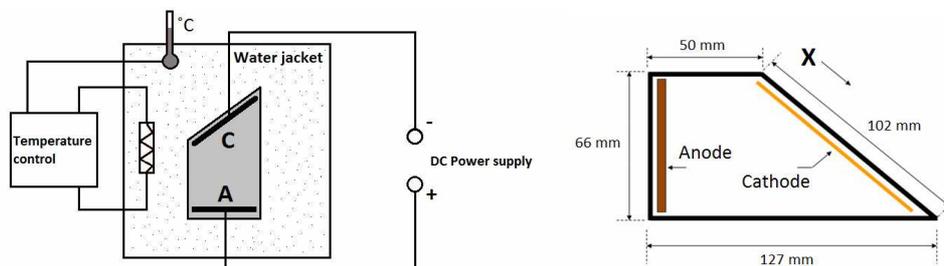


Figure 2. Schematic illustration of a home-made laboratory Hull cell (top view) placed in a water bath for temperature control. The anode plate (A) was a pure tin sheet and the cathode plate (C) was a pure copper foil, both immersed vertically in the electrolyte solution

Table 1
Characterization of the tin electroplated copper foils prepared in the Hull cell via deposition at a constant cell current of 1 A at 30 °C.

Sample No.	Position on the cathode plate, X (mm)	Calculated cathode current density, j (A/dm ²)	Appearance of the tin deposit
Sample 1	84	0.26	Light silvery grey
Sample 2	73	0.58	Light silvery grey
Sample 3	68	0.74	Shiny silvery
Sample 4	60	1.02	Shiny silvery
Sample 5	59	1.06	Smooth grey
Sample 6	50	1.44	Smooth grey
Sample 7	49,5	1.46	Smooth grey
Sample 8	45	1.68	Smooth grey
Sample 9	43	1.78	Smooth grey
Sample 10	35	2.25	Smooth grey
Sample 11	33	2.38	Dull grey
Sample 12	25	3.01	Dull grayish black
Sample 13	17	3.89	Microgranulous dull grey-black
Sample 14	7	5.91	Microgranulous dull blackish

Cathode size: 100 mm x 75 mm
 Anode size: 75 mm x 50 mm x 7.5 mm
 Solution volume: 267 ml

Current distribution is based upon the formula:

$$-j=I(5,1-5,24 \cdot \lg X),$$

where

j = current density (A/dm²)

I = total current (A)

X = distance from the high current density end of the panel (mm)

2.2. Instrumentation

2.2.1. Optical stereomicroscopy

Stereomicroscopes are variants of optical microscopes, designed for qualitative depth profiling. These devices allow the observation of sample images with high spatial resolution, typically using light reflected from the surface of an object, rather than transmitted through it. This imaging method provides a three-dimensional visualization of solid samples even with complex surface topography, where the three-dimensional view offers special advantages for the detailed analysis of the surface profiles. For this purpose, we used a Zeiss Discovery V12 Stereo Microscope. The SteREO Discovery series incorporates three options, with zoom factors of 8, 12 and 20; whereby the V12 set offers a motorized 12:1 zoom, with excellent depth resolution.

2.2.2. Scanning electronmicroscopy

The morphology of the samples was investigated by using a Zeiss EVO MA type Scanning Electron Microscope, equipped with an EDAX Genesis APEX 2 system for energy-dispersive X-ray microanalysis. Microphotographs of 1000x magnification were obtained with BSE (“back scattered electrons”) method. This technique allowed the precise mapping not only of sample topography, but of compositional contrasts as well.

2.2.3. Glow Discharge Optical Emission Spectroscopy (GD OES) with Depth Profiling

Thin film analysis with various sputter-depth-profiling techniques is based on the erosion of material surfaces as a result of energetic particle bombardment (mostly ion bombardment), whereby the material (i.e. the constituting atoms) is being removed continuously as a function of sputtering time. These analytical techniques can be divided in two main groups: “removed-matter” techniques and “remaining-surface” techniques. In the “remaining-surface” type analytical techniques (e.g. XPS – photoelectron spectroscopy, AES – Auger electron spectroscopy), the surface obtained by sputtering is analysed; while in the “removed-matter” techniques (e.g. secondary ion mass spectrometry – SIMS, laser ablation inductively coupled plasma mass spectrometry – LA ICP MS, glow discharge optical emission spectrometry – GD OES and glow discharge mass spectrometry – GD MS), the analysis of the sputtered material as a function of sputtering time allows the determination of the compositional distribution of a thin film (formed from the extracted material on a suitable substrate) against the distance from the original (sample) surface [3].

In our case, the GD OES analysis was performed with a GD-Profilier2 instrument manufactured by HORIBA Jobin Yvon (Longjumeau, France). This instrument is equipped with a radiofrequency generator (operating at 13.56 MHz frequency) and a standard HJY glow-discharge source with an internal anode diameter of 4 mm, which corresponds to the exact surface area detected on the tin coated copper foil samples in each GD OES investigation process (as listed in Table 1). GD operation mode with “*constant pressure-constant forward power*” setting (450 Pa pressure, 40 W *rf*-forward power) was used for each experimental series. After the proper mode of operation had been set – i.e. the discharge and sputtering conditions were determined in a way to optimize the crater shape – the glow discharge process was initiated. The measured experimental curves of the light intensities emitted by the respective elements (i.e. the elements present in the sampled tin deposit to the depth of the copper substrate) were being recorded (Figure 3).

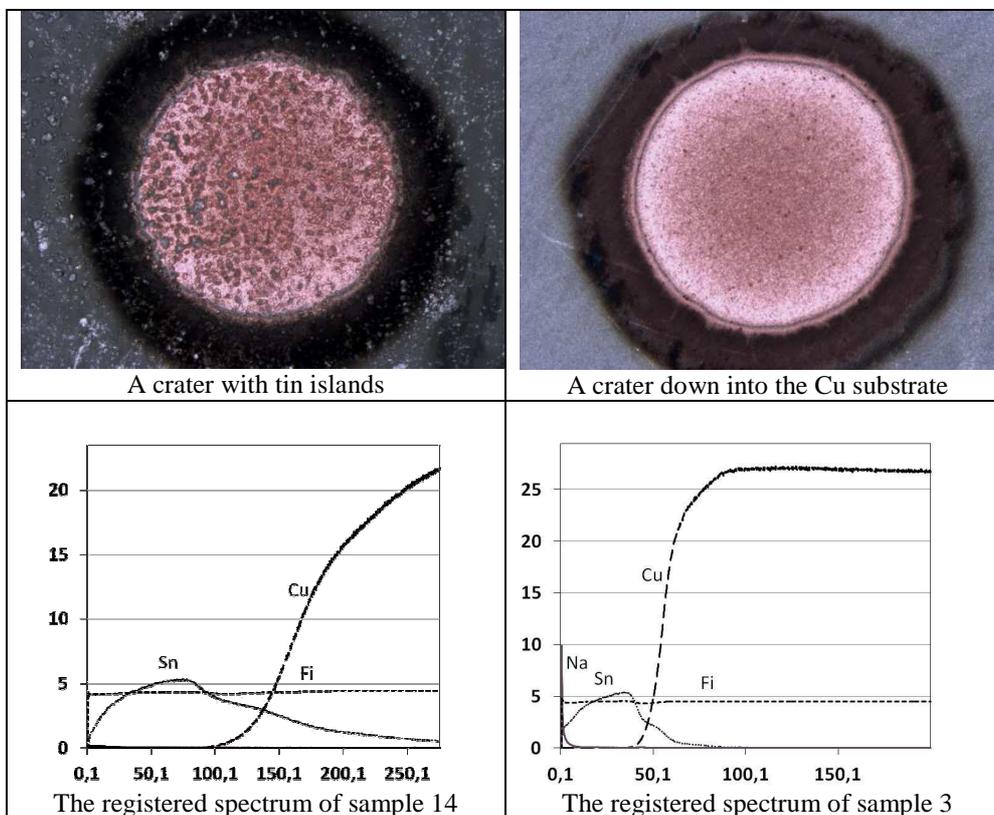


Figure 3. Above: Stereoscopic images ($N = 50\times$) of the craters formed by glow discharge (GD) argon sputtering during the GD OES depth profile analysis of tin electroplated samples deposited on copper foils/substrates. Below: spectrums indicating the light intensities of emitted photons (vertical axis) as a function of sputtering time (horizontal axis)

3. Results and discussion

The studied tin electroplated copper sample sheets (measured total surface area: ~ 100mm x 75 mm), were characterized by light greyish smooth surface, except for the region where deposition was taking place at the highest current densities (See Table 1). In this region, the tin deposit was blackish dull and grainy. The GD OES depth profile analysis was performed along the longer edge of the samples, in the middle region towards the grainy zone. Starting from the side with lower current densities, 14 GD sputtering experiments were performed on each tin electroplated specimen, in about 1 cm steps between the craters formed. Three representative set of steps are shown in Figure 4, with the results obtained from the GD OES experiments.

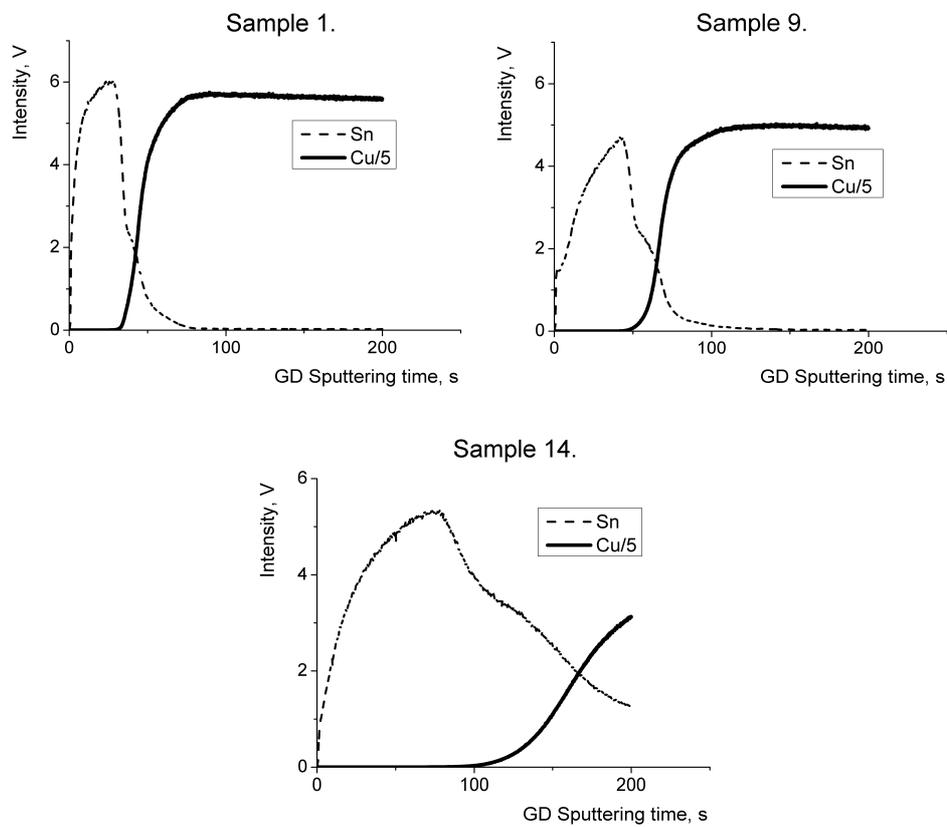


Figure 4. GD OES depth profile analysis. Spectra recorded for the respective samples at increasing current densities and uniform sputtering time intervals for each GD sputtering experiment

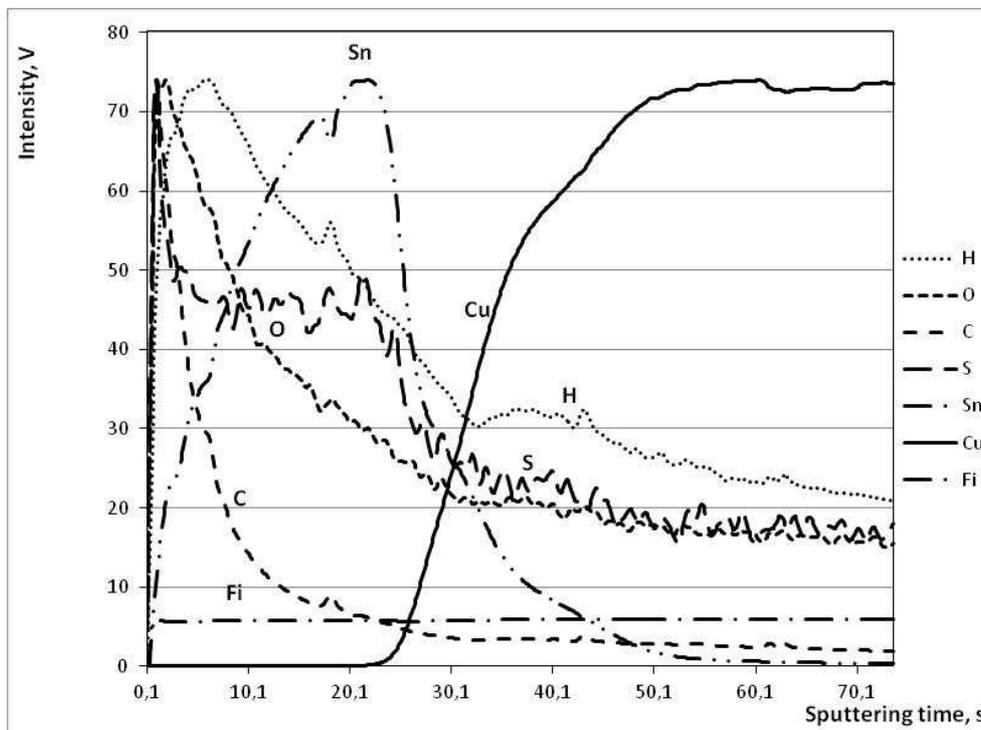


Figure 5. GD OES signal intensities maximized (except for copper) to show the constituting elements (Sn, C, O, H and S) of the tin electroplating bath slightly incorporated in the thin tin deposit.

As it is apparent from Figure 5, the outermost surface of the tin plated sample was supposedly exposed to slight oxidation in air and got slightly contaminated with some carbon containing material (e.g. finger print). Internally, the presence of evenly distributed sulfur is also recognizable.

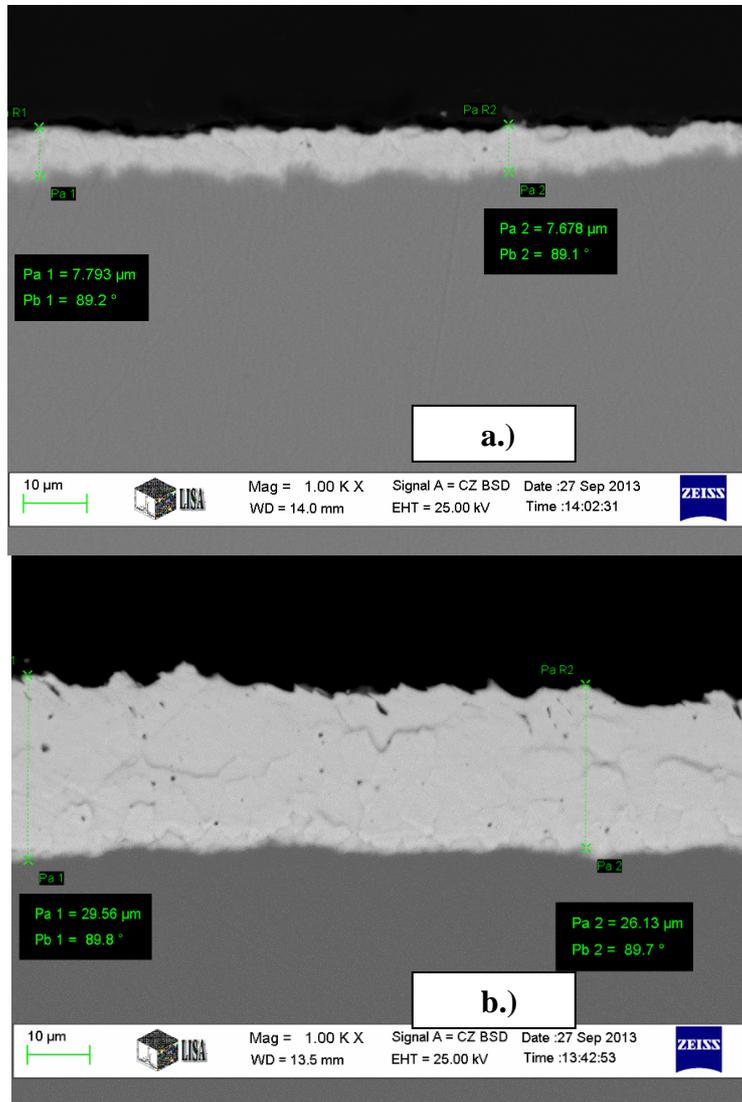


Figure 6. a–b) Cross section SEM images of two tin electroplated samples:
a) thin tin layer; b) thick tin layer

In Figure 6, the grain structure of the deposits is seen to be quite fine and equiaxed, not columnar. Though, at some regions a few small voids can be observed. These can be attributed to a certain extent of hydrogen co-deposition accompanying the cathodic reduction of tin. With the occasional mixing of the plating solution or the vibration of the cathode plate, the presence of hydrogen could most probably have been reduced. However,

in a small Hull cell like ours, such mechanical modifications were not possible to implement. Based on the observed microstructure of the thin tin layer, no risk of whiskers formation is expected – as it follows from recent reports on the explanatory results of spontaneous whiskers growth [2]. Moreover, the thin tin layer deposited from the given industrial methane-sulfonic-acid type tin plating bath did not show any proneness to Cu-Sn intermetallic compound formation. Of course, the probability of Sn-Cu intermetallics formation cannot be excluded if, for example, the deposited layer produced at ambient ($\sim 30^\circ$) temperature would be exposed to higher temperatures for longer periods of time.

Summary

In this paper, we presented some details of the coating structures, and the effects of current density distribution on structure formation of thin tin layers formed on pure copper sheets during our laboratory electroplating experiments. At higher (i.e. $> 2.5 \text{ A/dm}^2$) current densities the thin tin deposits were darker greyish and more microgranulous (slightly spongy). However, the tin deposits microstructure were always (at least within the studied current range of about $0.3\text{--}4 \text{ A/dm}^2$) quite fine and equiaxed, not columnar. Right after deposition no sign of Sn-Cu intermetallics formation could be observed. Nevertheless, slight incorporation of sulphur was detected by the GD OES depth profile measurements in the deposits so obtained from the given and highly acidic methane sulfonic acid tin industrial electroplating bath.

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