Influence of M12 Organic Additive On the Electrodeposition of Tin From an Acid Sulfate Solution

by S. Bakkali, T. Jazouli, M. Cherkaoui, M. EbnTouhami, N. El Hajjaji & E. Chassaing*

The electrodeposition of tin from acid sulfate solutions was investigated. The effect of S-dodecyl-mercaptobenzimidazol additive (M12) was studied using an electrochemical quartz crystal microbalance. In the presence of M12, the overvoltage for hydrogen evolution was markedly increased. Tin discharge was controlled by mass transfer; the diffusion coefficient of the Sn(II) species was smaller than in pure acid sulfate solutions. The deposit morphology was much smoother and brighter and no dendritic growth was observed over a wide potential range. This was associated with a change in the preferred orientation of the tin films.

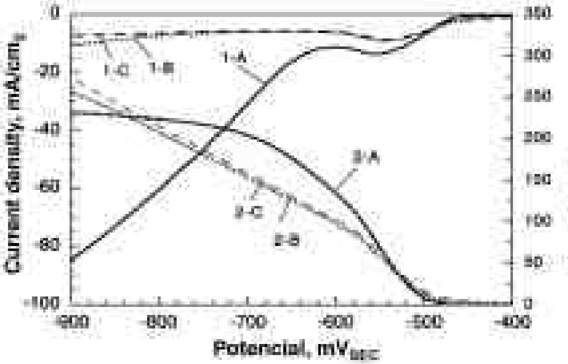

Fig. 1—Cathodic polarization results with EQCM (scan rate: 10 mV/s); Curves 1-A, B, C: Current density responses for electrolytes A, B and C, respectively; Curves 2-A, B, C: Mass change responses for electrolytes A, B and C, respectively.

Tin coatings are widely used to improve corrosion resistance, enhance appearance and/or increase solderability.[1] The most widely used process is electrodeposition from acid stannous sulfate solutions,[1] though sulfonic acid solutions are also used, especially for tin plate.[2] However, in acid baths, tin is electrodeposited with little activation polarization in the absence of additives.[3] The deposits are dendritic or needle-like,[3-11] which however, may have application in microelectronics.[12] A great number of additives have been investigated,[8] such as surface active agents[3] and aromatic carbonyl compounds.[4-6,9]

Nuts & Bolts: What This Paper Means to You

Acid stannous tin baths are used extensively, but require organic additives to suppress dendritic (whisker) growth, both as-deposit-ing and in service. The effect of using a new additive, S-dodecyl-mercaptobenzimidazol (M12) was studied. The results point toward a smoother, brighter deposit with a tendency toward reduced dendrite (i.e., whisker) growth.

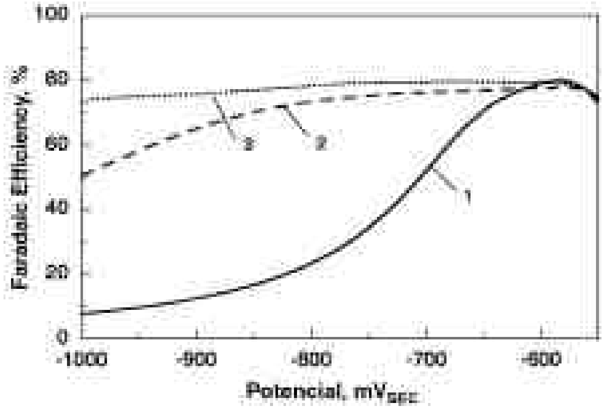

Fig. 2—Faradaic efficiencies as a function of polarization; Curves 1, 2, 3 recorded for electrolytes A, B and C, respectively.

In the present work, we investigated the influence of a new organic additive, S-dodecyl-mercaptobenzimidazol (M12), with the aim of preparing deposits with good solderability for microelectronic purposes. For these applications, the deposits have to be bright and smooth. S-dodecyl-mercaptobenzimidazol is a precursor of surfactant molecules and may be used as corrosion inhibitor or fungicide.[13] Our study was carried out by means of voltammetry, using an electrochemical quartz crystal microbalance and rotating disc electrode. The characterization of the deposits was made by scanning electron microscopy and X-ray diffraction.

Experimental Procedure

The investigation was carried out using a classic three-electrode cell. The temperature was maintained at 20 ± 1°C (68 ± 1.8°F). The solutions were de-aerated prior to each experiment by nitrogen bubbling. They were either still or stirred by a magnetic stirrer. The reference electrode was a saturated calomel electrode (SCE). The auxiliary electrode was a platinum coil or a tin plate. The working electrode was either the crystal of an electrochemical quartz crystal microbalance** or a rotating disk electrode (copper or iron). The disk surface was polished to a 3-µm finish, degreased and etched prior each experiment.

The composition of the various electrolytes investigated is given in Table 1. The S-dodecyl-mercaptobenzimidazol

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*Corresponding Author:
Elisabeth Chassaing
Centre d'Etudes de Chimie Metallurgique
15 rue Georges Urbain
94407 Vitry-sur-Seine Cedex, FRANCE
E-mail: elisabeth.chassaing@glvt-cnrs.fr

** *Maxtek PM 700, Maxtek, Inc., Santa Fe Springs, CA 90670*

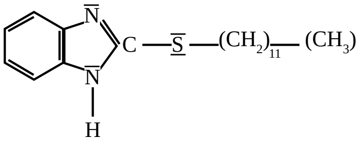
Table 1
Composition of the Various Electrolytes

Electrolyte	SnSO, M/dm^3	H_2SO_4, M/dm^3	Absolute C_2H_5OH, vol%	M12 Additive, M/dm^3
A	0.14	0.56	0	0
B	0.14	0.56	20	0
C	0.14	0.56	20	0.156 x 10^{-3}
A'	0.0467	0.118	0	0
B'	0.0467	0.118	12.5	0
C'	0.0467	0.118	12.5	1.05 x 10^{-5}

Table 2
Total, i_G, & Partial Current Densities, i_{Sn}, i_H, for Tin Deposition & Hydrogen Evolution (mA/cm^2) at two Potentials

Electrolyte		E = -600 mV$_{SCE}$			E = -700 mV$_{SCE}$		
		i_G	i_{Sn}	i_H	i_G	i_{Sn}	i_H
A	No stirring	11.3	8.9	2.4	31.1	16.0	15.1
B	No stirring	6.4	4.9	1.4	6.2	4.7	1.5
	Mech. stirring	16.2	12.0	4.1	23.8	18.7	5.1
C	No stirring	6.1	4.9	1.3	5.8	4.6	1.2
	Mech. stirring	12.5	8.9	3.6	14.2	11.2	3.0

was prepared[***] by condensation of 2-mercaptobenzimidazole with bromododecene in the presence of tetra-n-butylammonium as catalyst.[13] The formula of M12 is:



Since M12 is insoluble in water, it was first dissolved in ethanol. The basic electrolyte, denoted Electrolyte A in Table 1, contained stannous sulfate (0.14 M/dm^3) and sulfuric acid (0.56 M/dm^3). To determine the effect of ethanol, the electrolyte denoted B, identical to electrolyte A plus 20 vol% of ethanol, was investigated. The electrolyte, labeled C, contained tin sulfate and sulfuric acid in the same concentrations as electrolyte A plus 1.56 x 10^{-4} M/dm^3 M12 and 20 vol% ethanol. Dilute electrolytes were used to characterize the diffusion behavior of the Sn(II) species (Electrolytes A', B', C' - Table 1).

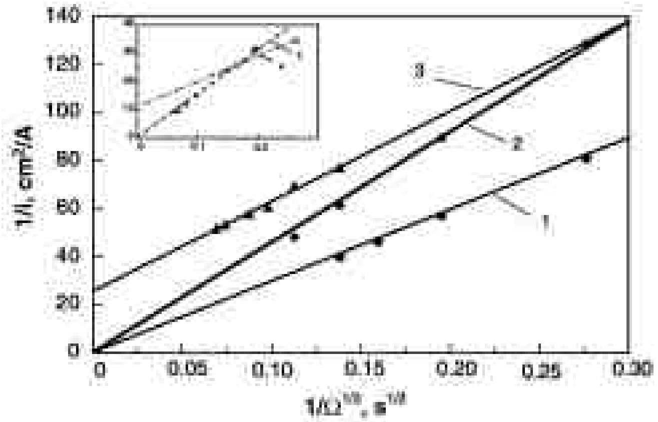


Fig. 4—Koutecky-Levitch plots: Curve 1, Electrolyte A' (E = -630 mV$_{SCE}$); Curve 2, Electrolyte B' (E = -750 mV$_{SCE}$); Curve 3, Electrolyte C' (E = -850 mV$_{SCE}$). In insert: Curve 4, Electrolyte A (E = -600 mV$_{SCE}$); Curve 5, Electrolyte C (E = -800 mV$_{SCE}$).

SEM observations were carried out using a high resolution-field-emission microscope.[****] Classical θ/2θ x-ray diffraction was performed using a diffractometer equipped with a cobalt anticathode ($\lambda K_{\alpha 1}$ = 0.17889 nm).

Results

Polarization Studies

To characterize the deposition of tin a voltammetric investigation was carried out using an electrochemical quartz crystal microbalance (EQCM) with a scan rate of 10 mV/s. Figure 1 shows the cathodic polarization curves and the mass changes for the three solutions. All polarization curves showed a peak for a potential close to -550 mV$_{SCE}$ related to the diffusion-controlled reduction of the stannous species. For the basic electrolyte without the additive (curve 1-A), the current increased rapidly with cathodic polarization. In the presence of alcohol (curve 1-B) or in the presence of alcohol and M12 (curve 1-C), the peak current was slightly reduced. For potentials ranging between -650 and -1000 mV$_{SCE}$, the current was nearly constant and remained markedly smaller than in the absence of the additive.

The response of the EQCM showed that the deposition started at a potential close to -450 mV$_{SCE}$ for all the solutions. For electrolyte A, the mass increased rapidly with polarization up to 700 mV$_{SCE}$ (curve 2-B). For more negative potentials, the mass increased no further because of the formation of non-adherent dendrites, which were stripped off the electrode. By contrast, in electrolytes B and C, the mass increased regularly (curves 2-B, 2-C) and adherent deposits were formed.

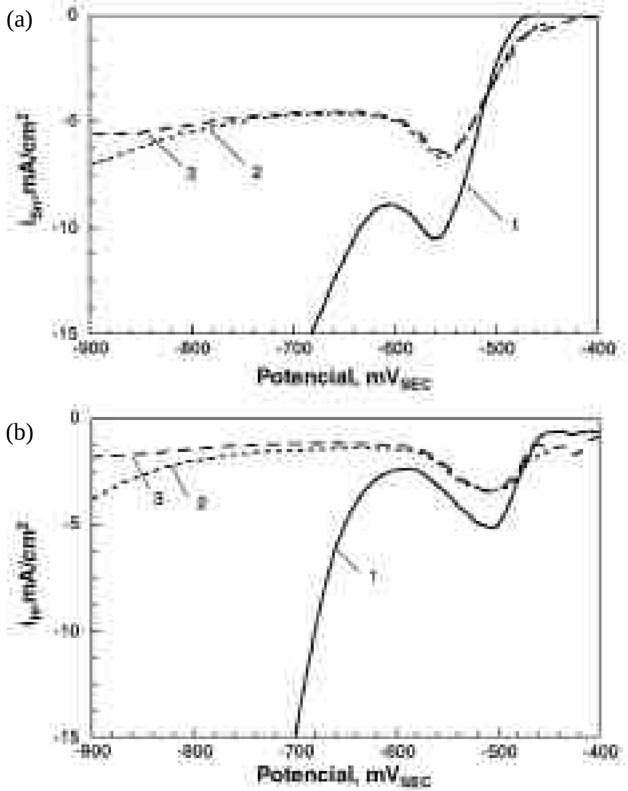


Fig. 3—(a) Partial current density for tin deposition; Curves 1, 2, 3 recorded for electrolytes A, B and C respectively.
(b) Partial current density for hydrogen evolution; Curves 1, 2, 3 recorded for electrolytes A, B and C, respectively.

[***] *Laboratory of Organic Synthesis and Reactivity, University Ibn Tofail, Kenitra, Morocco.*

[****] *LEO 1530, LEO Electron Microscopy Ltd., Cambridge, UK.*

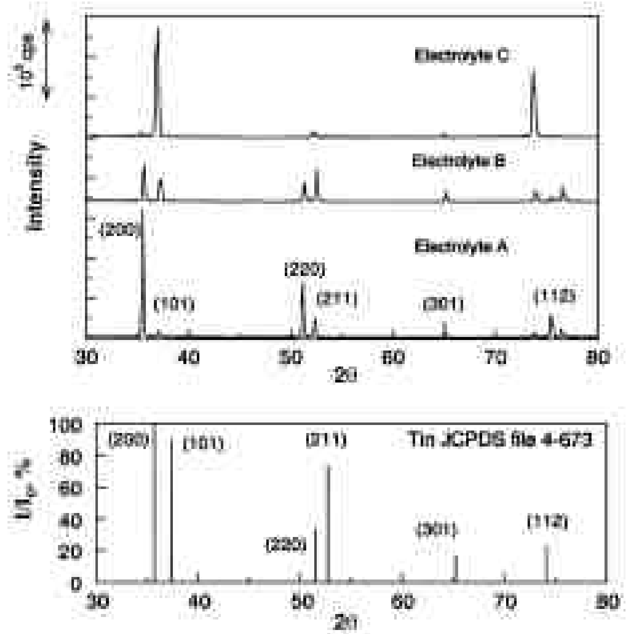


Fig. 5—(a) X-ray diffraction patterns of films deposited from electrolytes A, B and C. (b) Reference pattern of tin (JCPDS file 4-673).

The cathodic current efficiency was calculated from the results of the EQCM, using Faraday's Law. In the absence of additive, the efficiency was about 80% at a potential of -600mV$_{SCE}$, but decreased at larger overpotentials (Fig. 2, curve 1). For electrolytes B and C, the efficiency remained constant at more negative potentials, especially for electrolyte C, containing both alcohol and M12 additive (Fig. 2, curves 2 and 3).

The partial currents for the deposition of tin and for the hydrogen evolution reaction were calculated from the results of the EQCM. Figure 3a shows that, in baths B and C (curves 2 and 3, respectively), at -600 mV$_{SCE}$, the partial current for tin deposition was approximately half that measured in the basic electrolyte (curve 1). At -700 mV$_{SCE}$, the partial current value was one-third of the basic electrolyte value. This shows that alcohol and M12 had an inhibiting effect on tin discharge. Figure 3b clearly shows that, in the presence of the additives, the overvoltage for hydrogen evolution was markedly increased. In addition, the presence of a current peak in the same potential range as for tin deposition, indicates that the reduction of the protons was involved with tin discharge.

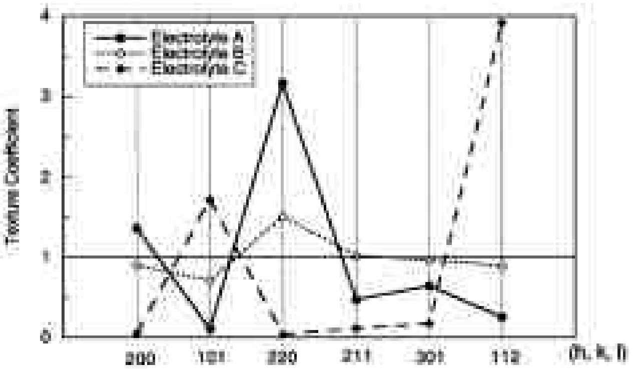


Fig. 6—Texture coefficient of films deposited from electrolytes A, B and C.

Influence of Mass Transfer

For all the solutions, mass transfer partly controlled the deposition kinetics. In the presence of mechanical stirring, the current density and the deposited mass were increased. Table 2 summarizes the results. Mechanical stirring markedly increased the total current as well as the partial currents for metal deposition and hydrogen evolution. Hence the Faradaic efficiency was not markedly changed.

Rotating disc electrode studies (0-2500 rpm) were carried out to estimate the diffusion coefficients for these electrolytes and for the dilute solutions (solutions denoted with prime index, Table 1). Koutecky-Levich plots were drawn (Fig. 4).[14] For electrolytes A and A' (curve 1), the apparent diffusion coefficient was 5.0 ± 0.5x10^{-6} cm^2/s, i.e., on the same order as for deposition from sulfonate solutions.[12] For electrolytes B and B' (curve 2), the apparent diffusion coefficient was approximately half of the A-A' value (2.3 ± 0.5x10^{-6} cm^2/s). For the electrolytes containing the M12 additive, the intercept was not zero, indicating a kinetic contribution to the deposition current. In electrolytes C and C' (curve 3), the apparent diffusion coefficient was dependent on the potential, as already observed in sulfonate solutions.[12] This occurred when Sn(II), before charge transfer, had to diffuse through an organic film whose orientation would change with potential.[12] The diffusion coefficient was also greater in the dilute solution, C' (2.7-3.3 x10^{-6} cm^2/s), than in the more concentrated one, C (2.0-3.0 x10^{-6} cm^2/s). This might indicate interactions between the stannous species and the M12 compound.

Table 3
Lattice Parameters of the Films Deposited from the three Electrolytes Compared to that of the Reference Pattern

Lattice Parameter, nm	JCPDS File 4-673	Electrolyte A	Electrolyte B	Electrolyte C
a	0.5831	0.587	0.585	0.589
c	0.3182	0.321	0.319	0.321

Morphology & Structure

Tin layers, 10 µm (394 µ-in.) in thickness, were deposited at 4.0 A/dm^2 (37.2 A/ft^2) on an iron disc rotating at 2000 rpm, from the three solutions. They were then examined by scanning electron microscopy and X-ray diffraction about a week after their preparation.

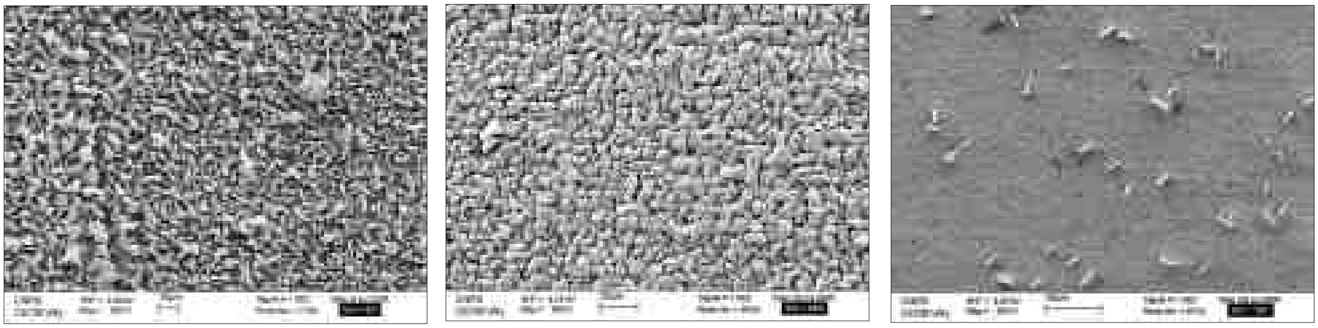


Fig. 7—Scanning electron micrographs of films deposited from electrolytes A, B and C, magnification 500X.

The X-ray patterns are shown in Fig. 5, together with the JCPDS file of tin (No. 4-673). They all exhibit a tetragonal structure. The lattice parameters of the deposited tin films were greater than that for bulk tin (Table 3). The figure clearly indicates that the texture changed in the presence of the additives. For each diffraction peak, we calculated the ratio

$$(I_{(hkl)}/I_0)/(1/n)\sum(I_{(hkl)}/I_0),$$

where $I_{(hkl)}/I_0$ is the ratio of the intensity of the line with the corresponding line of the reference pattern (Fig. 6). The least textured sample came from bath B containing alcohol. The film deposited from the electrolyte A (without additives) showed a strong (200) preferred orientation whereas the layer deposited from bath C with M12 showed a strong (101) preferred orientation.

Further, Fig. 5 shows relatively broad lines indicating that the films had a small grain size. According to Scherrer's formula, the films deposited from electrolyte A have grain sizes on the order of 100 nm. As often observed, the grain size was further reduced in the presence of alcohol (70 nm) and M12 (55 nm).

Figure 7 shows that the morphologies of the films were quite similar and rather irregular for layers deposited from electrolyte A without additive or from bath B with alcohol (Fig. 7a, b). By contrast, in the presence of M12, the morphology was much more regular and smooth (Fig 7c). The films were quite stable, and no dendrite formation was observed even after long storage periods at ambient temperature in the laboratory atmosphere.

Conclusions

A new additive, S-dodecyl-mercaptobenzimidazol, was used to electrodeposit tin from acid stannous solutions.

Electrochemical investigations showed that the additive did not shift the deposition potential, which is often observed in the presence of additives.[3] It reduced the partial current for tin deposition. In addition, it markedly increased the overvoltage for hydrogen evolution, and thus increased the deposition range for the deposition of compact films.

The additive had a marked effect on the preferred orientation of the deposits and the films were much brighter. Scanning electron microscopy showed that, with the additive, much smoother layers were obtained, exhibiting a more regular morphology.

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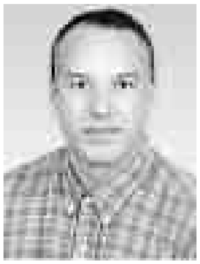
About the Authors

S. Bakkali



Dr. T. Jazouli

Dr. M. Cherkaoui

Dr. M. Ebntouhami

Dr. N. Hajjaji

Dr. E.Chassaing

Said Bakkali is a PhD student at the Faculty of Sciences, Ibn Tofail (Kenitra, Morocco).

Dr. Talha Jazouli is a permanent staff member of the Laboratory of Organic Synthesis and Reactivity at the University Ibn Tofail (Kenitra, Morocco). He holds MSc (Rabat, 1983) and PhD (Paul Sabatier University, Toulouse, France, 1987) degrees. His main interests are organic precursors of surfactant molecules and organic corrosion inhibitors and fungicides.

Dr. Mohammed Cherkaoui is professor and head of the Laboratory of Electrochemistry and Surface Treatments at the Faculty of Sciences, University of Kenitra (Morocco). He holds MSc (Rabat, 1984), PhD (University of Paris, 1987) and Doctor of Science (University of Kenitra, 1993) degrees. His main interests are electrodeposition, properties of metallic coatings and the behavior of silicon in fluoboric solutions

Dr. Mohamed Ebntouhami is professor and permanent staff member of the Laboratory of Electrochemistry and Surface Treatments at the Faculty of Sciences, University IbnTofail (Kenitra, Morocco). He holds MSc (Kenitra, 1992) and Doctor of Science (Kenitra, 2000) degrees. His main interests are electrodeposition and properties of metallic coatings, corrosion and protection of metals.

Dr. Najat Hajjaji is professor and head of the Laboratory of Organic Synthesis and Reactivity at the University Ibn Tofail (Kenitra, Morocco). She holds a PhD (Paul Sabatier University, Toulouse, France, 1983) and a Doctor of Science (Kenitra, 1987) degree. Her main interests are synthesis and aggregation of surfactants, the synthesis of corrosion inhibitors and oil emulsions.

Dr. Elisabeth Chassaing is director of research at the Centre National De La Recherche Scientifique (CNRS) and permanent staff member of the Centre d'Études de Chimie Métallurgique-CNRS (France). She is head of the Corrosion Research Group there. She holds a Doctor of Science (University of Paris, 1975). Her main fields of interest are electrocrystallization of metals and alloys and corrosion protection.