

Additive effects on tin electrodepositing in acid sulfate electrolytes

Fa-xin Xiao¹), Xiao-ni Shen¹), Feng-zhang Ren¹), and Alex A. Volinsky²)

1) School of Materials Science and Engineering, Henan University of Science and Technology, Luoyang 471003, China

2) Department of Mechanical Engineering, University of South Florida, Tampa FL 33620, USA

(Received: 10 June 2012; revised: 30 July 2012; accepted: 8 August 2012)

Abstract: The effects of additives on the stannous reduction of an acid sulfate bath were investigated using cyclic and linear sweep voltammetry, electrochemical impedance spectroscopy (EIS), and microstructure analysis. In the absence of additives, tin coatings are rough, and the tin electrodepositing is a single-step reduction process accompanied by hydrogen gas evolution. The addition of tartaric acid produces a slight reduction in the peak current of stannous reduction and has an appreciably positive effect on the stability of the acidic tin bath. Both benzylidene acetone and polyoxyethylene octylphenol ether hinder the stannous reduction and greatly suppress the hydrogen gas evolution. Formaldehyde slightly decreases the peak current density of stannous reduction and serves as an auxiliary brightener in the acid sulfate bath. The presence of mixed additives greatly suppresses the stannous reduction and hydrogen gas evolution and consequently produces a significantly smoother and denser tin coating. The (112) crystal face is found to be the dominant and preferred orientation of tin deposits.

Keywords: electrodepositing; tin; additives; stannous reduction

1. Introduction

Pure tin electroplating has become the most popular surface coating process for lead-free electronic components because of its good wettability, solderability, compatibility, as well as its low cost and ease of manufacture [1-2]. Tin and its alloys can be electrodeposited from various electrolytes, including aqueous fluoroborate, sulfate, and methanesulfonate solutions [3-5]. In the past ten years, the methanesulfonate-based electrolyte was favored because of the low corrosivity and nice ability to dissolve metals that are insoluble in other organic or mineral acids [5-7]. Multiple research projects aimed at promoting industrial applications of this system, especially in printed circuit board (PCB) manufacturing. Compared with methanesulfonic acid, sulfuric acid has many advantages, including its environmental friendliness and relatively low cost [5-6]. Therefore, the acid sulfate electrolyte has become increasingly popular for tin electrodepositing, being an ideal choice for the next generation of electronic components [8-10]. The tin deposition process is rather fast in the absence of additives, but the deposits obtained under such conditions are mostly porous, coarse, and poorly adherent to the tin

sulfate electrolyte [11-13]. Consequently, organic additives are necessary if smooth and dense films are to be obtained.

Additive examples may include surfactants to promote the electrode reaction, oxidation inhibitors to reduce the formation rate of stannic ions [12], grain refiners to produce whiskers-free or dendrite-free coatings, and brighteners to obtain matte or bright deposits. Carlos *et al.* [12] investigated the effects of tartrate content on the aging and deposition condition of copper-tin electrodeposits and found that the addition of the tartrate in the plating bath caused a marked change in the morphology of Cu-Sn films obtained galvanostatically. Xiao *et al.* [14] found that the additives of formaldehyde and polyoxyethylene octylphenol ether were able to significantly refine the grains and change the morphology of the Sn coating, and the tin coating obtained from the bath with benzylidene acetone was significantly fined and in flake-type growth. Martyak and Seefeldt [7] proposed that the addition of phenolphthalein to solutions already containing glycol additives resulted in a smooth matte tin deposit. In addition, it is further regarded that a bright and fine tin coating can be achieved by adding additives containing aldehyde, carbonyl and vinyl

Corresponding author: Fa-xin Xiao E-mail: hkdxfx@yahoo.com.cn

groups [15-16]. Until now, most researches focused on using additives in the acid sulfate electrolyte to produce lustrous or bright deposits, yet the role of organic additives has not been fully understood.

The aim of this work is to study the role of additives, including tartaric acid, benzylidene acetone, polyoxyethylene octylphenol ether and formaldehyde, in the stannous reduction of acid sulfate baths using electrochemical methods and deposit morphology analysis.

2. Experimental

The components of the basic solution are given in Table 1. The basic solution was made up by dissolving stannous sulfate in a sulfuric acid solution. A controlled concentration of additives, including benzylidene acetone, polyoxyethylene octylphenol ether (30wt%), tartaric acid and formaldehyde (37wt%), was added in the basic solution to prepare samples for electrochemical tests. The solutions were filtered prior to testing and then heated to 25°C during the experiments.

Table 1. Components and their concentration of the basic solution

Component	Concentration/(g·L ⁻¹)
H ₂ SO ₄	125
Sn ²⁺	20

The electrochemical tests were carried out using a CHI-660C electrochemical workstation in an H-type electrolytic cell. All potentials were recorded versus a saturated calomel electrode (SCE). Cyclic voltammetry (CV) measurements were performed from -0.1 to -0.6 V versus SCE, where the scan was stopped at preselected positive voltages. Polarization measurements were made with a scan rate of 1 mV/s or 10 mV/s by using a Cu wire, with the diameter of 1 mm, as the working electrode and a large-area Pt film as the counter electrode. The impedance spectrum was measured at -0.43 V, with the frequency ranging from 0.1 Hz to 100 MHz.

The surface morphology of tin deposits was studied using a JEOL JSM-5610LV scanning electron microscope (SEM). The X-ray diffraction (XRD) patterns were acquired using a BRUX D8 X-ray diffractometer.

3. Experimental results and discussion

3.1. Stannous reduction of the additive-free tin solution

The CV curve of the additive-free tin solution with a scan rate of 10 mV/s is shown in Fig. 1. The cathodic polarization curve of stannous reduction with a scan rate of 1 mV/s is shown in Fig. 2.

It can be seen in Fig. 1 that the stannous reduction process is a single two-electron step from the stannous ion to metallic tin:



The tin electrodepositing starts at a nucleation potential of -0.43 V approximately, via an abrupt increase in current density, as the deposition potential moves negatively away from the equilibrium potential. Upon reversing the potential sweep from -0.6 to 0 V, a single oxidation peak is observed at -0.36 V (peak a'). This confirms a single two-electron oxidation step from metallic tin to the stannous ion according to the reverse of Reaction (1).

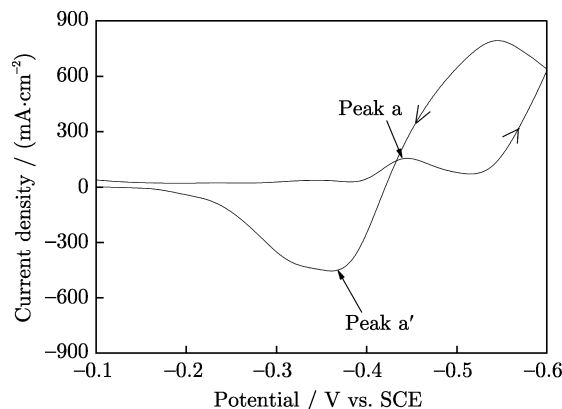


Fig. 1. CV curve of the additive-free tin bath with a scan rate of 10 mV/s.

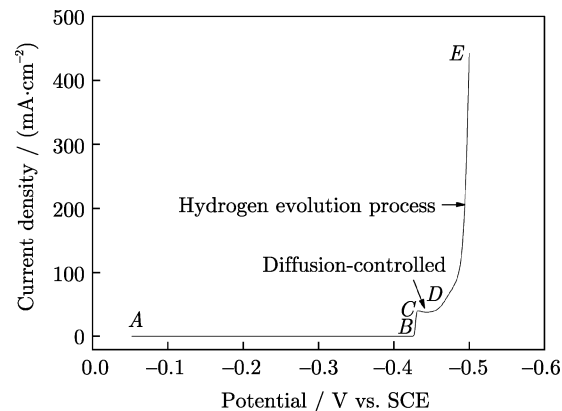


Fig. 2. Cathodic polarization curve of the additive-free tin bath with a scan rate of 1 mV/s.

Fig. 2 shows that the stannous reduction process of the additive-free solution can be divided into four stages. In region AB, the current density is nearly zero, and no reaction happens. Region BC, where the current density sharply increases from 0 to 39.8 mA/cm², demonstrates the stannous reduction process (Reaction 1). Region CD shows a slight decrease in current density, which indicates the diffusion-controlled process of stannous reduction (Reaction (1)). In region DE, the current density increases sharply past -0.46 V, which points to the hydrogen evolution reaction [7]:



Based on the cathode polarization curve, the peak current density, occurred at -0.43 V, is due to the consumption of stannous ions near the cathode. With continued polarization, the mass transfer is unable to replenish stannous ions at a rate that is sufficient to keep up with the reduction to metallic tin, and thus, the current density decreases. The current density rises again, starting at -0.46 V, due to a combination of stannous reduction and hydrogen evolution (Reaction 2). The electrochemical impedance spectroscopy (EIS) test was performed at -0.43 V for further study on the stannous reduction process, and the result is shown in Fig. 3. It shows that the stannous reduction is controlled by both electrochemical reaction and diffusion process as the Warburg impedance occurs in the low frequency range [17].

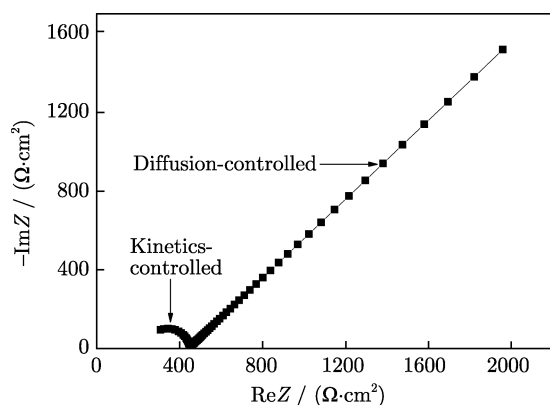


Fig. 3. Electrochemical impedance spectrum of an additive-free tin bath at -0.43 V.

3.2. Influence of tartaric acid on stannous reduction

The cathode polarizations were measured in the basic solution (Table 1) with various tartaric acid concentrations with a scan rate of 10 mV/s, and the results are shown in Fig. 4.

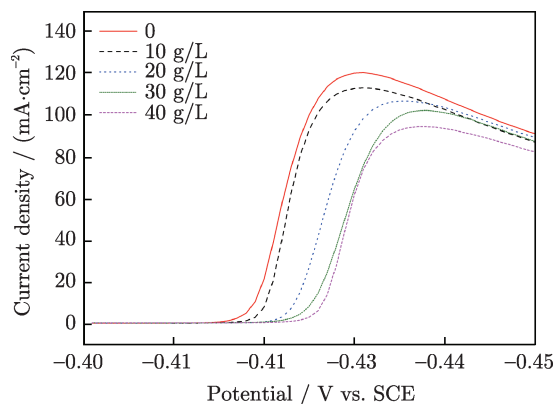


Fig. 4. Cathodic polarization curves of the basic solution with various concentrations of tartaric acid.

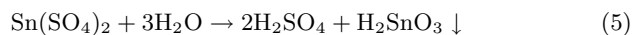
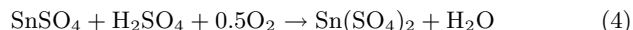
These curves show that the stannous reduction potential shifts to more negative values and the peak current density decreases with the increase in tartaric acid concentration. In an acid sulfate bath, the tartaric acid reacts with stannous ions (Sn^{2+}) to form a complex compound:

$$n\text{C}_4\text{H}_6\text{O}_6 + \text{Sn}^{2+} \rightarrow \text{Sn}[\text{C}_4\text{H}_6\text{O}_6]_n^{2+} \quad (3)$$

The presence of complex tin ions causes the free stannous ion concentration to reduce, which enhances the activation energy of tin deposition reaction. Consequently, the reduction peak potential shifts negatively, and the peak current density decreases. When the tartaric acid dosage exceeds 30 g/L, the complex reaction reaches saturation, and its influence on the tin reduction is not significant [16]. Therefore, the optimal tartaric acid concentration is 30 g/L in an acid sulfate bath.

In order to further confirm the complex reaction of tartaric acid with stannous ions, the oxidation of stannous ions was studied by exposing 1 L solution with a surface area of 100 cm² to atmospheric oxygen. A basic solution, as described in Table 1, and the solution in the presence of 30 g/L tartaric acid, were heated to and maintained at 80°C . Sludge formed on the bottom of the container in the basic solution, after being heated over 50 h. However, the bath in the presence of 30 g/L tartaric acid remained clear, even after 200 h of heating, and the sludge appeared at the bottom of the container after 250 h of heating. Therefore, the presence of tartaric acid has an appreciably positive effect in hindering the oxidation process.

In the sulfate-based solution, the oxidation of stannous salts and the subsequent hydrolysis are described by the following reactions:



Stannic ions in the electrolyte tend to precipitate as finely dispersed 'tin oxide' particles and can lead to sludge formation and instability of the electrolyte, as evidenced by the increase in solution turbidity [5]. The amount of free stannous ions in the bath decreases in the presence of tartaric acid due to Reaction (3), which suppresses Reactions (4) and (5), and hinders the tin bath decomposition. Therefore, the presence of tartaric acid improves the stability of the acidic tin electrolyte. It was also observed that this additive hindered the decomposition of the Cu-Sn bath, due to the longer storage time [12].

3.3. Influence of benzylidene acetone on stannous reduction

The influence of benzylidene acetone on the cathodic polarization curves of stannous reduction with a scan rate of 10 mV/s is shown in Fig. 5.

These curves show that the addition of benzylidene acetone has a pronounced effect on the deposition of tin. The stannous reduction peak potential shifts negatively, and the peak current density decreases with the

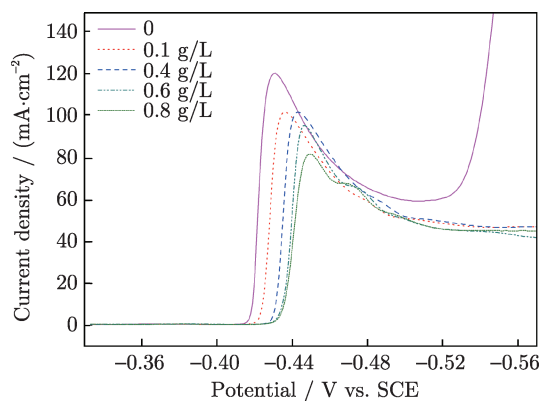


Fig. 5. Cathodic polarization curves of the basic solution with various concentrations of benzylidene acetone.

increase in benzylidene acetone concentration. Benzylidene acetone is an organic compound described by the $C_6H_5CH=CHC(O)CH_3$ formula. In this structure, although both *cis*- and *trans*-isomers are possible for the β -unsaturated ketone, only the *trans*-isomer is observed [14-15]. The presence of the benzene ring enhances the negative inductive effect of adjacent $-CH=CH-$ groups, which makes it easy to attract electrons to carbon atoms in the carbonyl group. Therefore, the positive electric charge of carbon atoms strengthens the carbonyl group, and its adsorption ability is consequently enhanced. Owing to this strong absorption of benzylidene acetone on the cathode surface, the tin electrodepositing and hydrogen gas evolution are hindered [14-15]. Therefore, a bright and smooth tin deposit, with fine crystallites, can be obtained by adding an appropriate amount of benzylidene acetone. It thus plays a role as a brightener and a grain refiner in the bath. The experiments showed that when the benzylidene acetone concentration exceeded 0.6 g/L, the tin coating was severely burned, due to the high local current density caused by the strong adsorption of benzylidene acetone. Therefore, the suitable benzylidene acetone concentration in a tin solution, in terms of quality, is 0.6 g/L.

3.4 Influence of formaldehyde on stannous reduction

The influences of formaldehyde on the cathodic polarization curves of stannous reduction with a scan rate of 10 mV/s are shown in Fig. 6.

It can be seen in Fig. 6 that the stannous reduction peak potential and the peak current slightly decrease with the increase in formaldehyde concentration. It was found that formaldehyde can increase the brightness range of the deposits, in the presence of benzylidene acetone, or polyoxyethylene octylphenol ether in a sulfate-based bath [14]. Kruglikov *et al.* [18] also found that a bright deposit formed only with a current density of 0.4 A/dm^2 in the

presence of benzylidene acetone, or sulfoalkyl polyalkoxylated naphthol in methyl sulfonate baths, whereas the value reached 6 A/dm^2 after formaldehyde was added. It is regarded that formaldehyde performs as an auxiliary brightener in the tin plating, which allows for the obtaining of bright deposits from a very wide current density range [19]. The appropriate formaldehyde concentration in the sulfate-based bath is 8 mL/L, owing to the relatively greater polarizability.

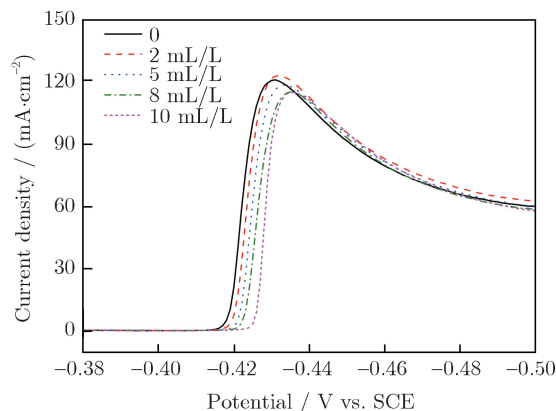


Fig. 6. Cathodic polarization curves of the basic solution with various formaldehyde concentrations.

3.5 Influence of polyoxyethylene octylphenol ether on stannous reduction

The influences of polyoxyethylene octylphenol ether on the cathodic polarization curves of stannous reduction with a scan rate of 10 mV/s are shown in Fig. 7.

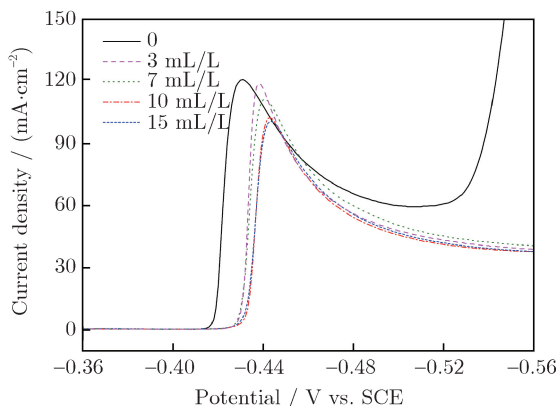


Fig. 7. Cathodic polarization curves of the basic solution in the presence of various concentrations of polyoxyethylene octylphenol ether.

As can be seen, when in the presence of polyoxyethylene octylphenol ether, the stannous reduction peak potential shifts negatively, the peak current density decreases, and the evolution of hydrogen is greatly suppressed. This effect is no longer significant when the dosage exceeds 10 mL/L.

Polyoxyethylene octylphenol ether is a well-known surfactant in the chemical industry, especially in the plating industry. Polyoxyethylene octylphenol ether piles up to form micelles on the electrode surface, due to its polymeric surfactant function [14-15]. Consequently, the absorption of this surfactant on the electrode surface hinders the hydrogen evolution and results in a great reduction in peak current density. When its dosage exceeds 10 mL/L, however, this adsorption is almost saturated. Therefore, a further increase of polyoxyethylene octylphenol ether has less effect on the tin electrodepositing. It was also found that a rod-like deposit was obtained, as there were many needle holes on the coating surface from the acid sulfate bath in the absence of polyoxyethylene octylphenol ether.

However, in the presence of polyoxyethylene octylphenol ether, a compact and smooth coating was obtained at a higher current density [14].

3.6. Influence of mixed additives on stannous reduction

The SEM images of the tin deposits at 30 mA/cm² and 25°C from the additive-free tin bath and the acid sulfate bath in the presence of mixed additives consisting of 30 g/L tartaric acid, 0.6 g/L benzylidene acetone, 8 mL/L formaldehyde, and 10 mL/L polyoxyethylene octylphenol ether are shown in Figs. 8 and 9, respectively. The influence of mixed additives on the cathodic polarization curve of stannous reduction is shown in Fig. 10.

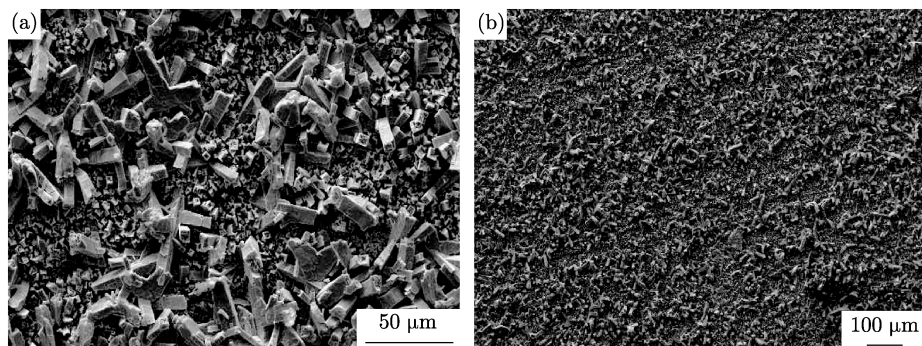


Fig. 8. SEM images of tin deposits obtained under the current density of 30 mA/cm² at 25°C from the additive-free bath.

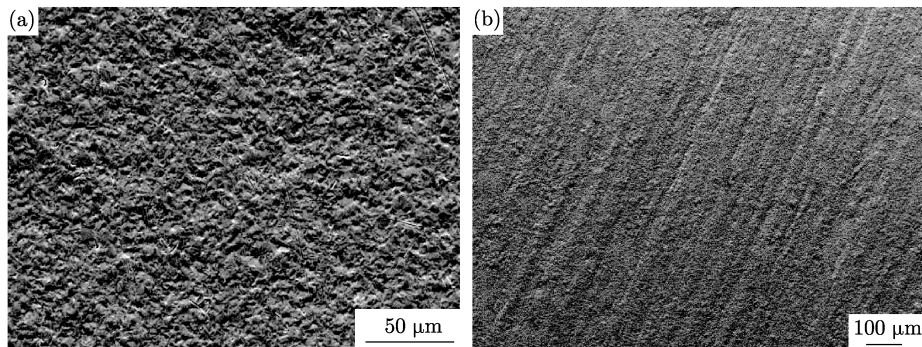


Fig. 9. SEM images of tin deposits obtained under the current density of 30 mA/cm² at 25°C from the acid sulfate bath in the presence of mixed additives.

It can be observed in Fig. 8 that many rod-like tin deposits are obtained on the coating surface from the additive-free solution. By comparison, Fig. 9 shows that the rod-like deposits disappear, allowing for uniform and smooth tin deposits. This result indicates that the mixed additives have great effects on the morphology and grain size of tin deposits in the acid sulfate bath.

Fig. 10 shows that, in the addition of mixed additives, the peak current of stannous reduction decreases from 121 to 11 mA/cm², and the peak potential shifts negatively. In addition, the hydrogen evolution is obviously suppressed.

The relationship between the nucleation rate (i) and the over potential (η) is given as follows [20]:

$$\ln i = A - B/\eta^2 \quad (\text{three-dimensional model}) \quad (6)$$

where i is the nucleation rate, A and B are constants, and η is the over potential of stannous reduction.

The electrochemical crystallization process consists of nucleation and grain growth. As a rule, rapid nucleation rate and slow grain growth rate are the causes of fine grains. According to Fig. 10, the peak potential shifts from -0.431 to -0.447 V, therefore the over potential increases by as much as 16 mV after the mixed additives

are added. As a result, the nucleation rate is accelerated sharply, based upon formula (6), which brings out fine grains and results in even and smooth tin deposits.

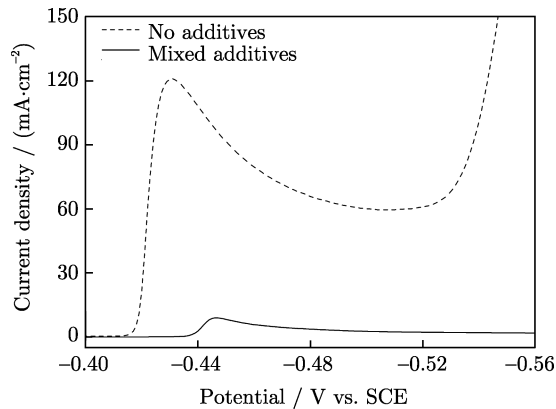


Fig. 10. Cathodic polarization curve of the acid sulfate bath with mixed additives.

3.7. XRD results of tin coatings

The phase composition of tin deposits plated in the acid sulfate bath with mixed additives was analyzed by XRD, and the pattern is shown in Fig. 11. The difference in diffraction reflection intensities of crystal faces between the plated tin coating and the standard body-centered cubic tin [21] is listed in Table 2.

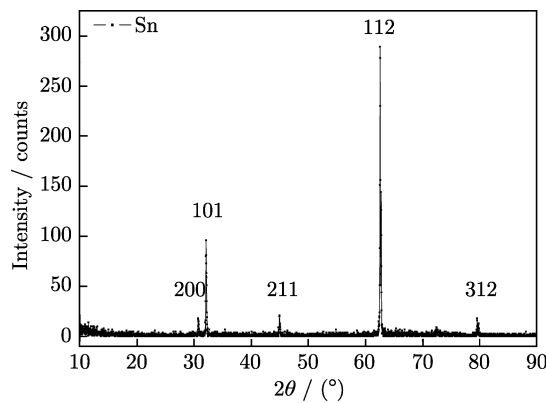


Fig. 11. XRD pattern of tin deposits obtained from the acid sulfate bath in the presence of mixed additives.

Fig. 11 shows that there are five main crystal faces indexed to tin deposits. In contrast with the body-centered cubic tin listed in Table 2, the (112) reflection intensity of the tin coating, as obtained from a bath with mixed addi-

Table 2. Difference in intensity of crystal faces between the tin coating with additives and body-centered cubic tin

Sample	$I_{(200)}$	$I_{(101)}$	$I_{(211)}$	$I_{(112)}$	$I_{(321)}$
Obtained coating	8.6	34.1	9.2	100	7.2
Standard tin	100.0	90.0	74.0	23.0	20.0

tives, is the highest. This shows that the deposited coating has a preferred (112) orientation.

4. Conclusions

(1) The stannous reduction from an additive-free tin bath (20 g/L Sn^{2+} and 125 g/L H_2SO_4) is a single-step process accompanied by hydrogen gas evolution. Moreover, it is controlled by both electrochemical reaction and diffusion process.

(2) The addition of tartaric acid produces a slight reduction in the peak current of stannous reduction and has an appreciably positive effect on hindering the oxidation of the tin bath. Both benzylidene acetone and polyoxyethylene octylphenol ether hinder the stannous reduction and greatly suppress the hydrogen gas evolution. Formaldehyde slightly decreases the peak current of stannous reduction and serves as an auxiliary brightener in the acid sulfate bath.

(3) In the presence of mixed additives, the cathodic peak current greatly decreases, and the hydrogen evolution is obviously suppressed. Also, smooth and compact tin deposits are obtained. The (112) direction is found to be the dominant and preferred orientation of tin deposits.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 50904023), the Natural Science Research Project of the Education Department of Henan Province (No. 2010B450001), the Innovation Scientists and Technicians Troop Construction Projects of Henan Province (No. 104100510005), and the Basic and Frontier Technologies Research Projects of Henan Province, China (No. 092300410064).

References

- [1] B. Illés, B. Horváth, and G. Harsányi, Effect of strongly oxidizing environment on whisker growth form tin coating, *Surf. Coat. Technol.*, 205(2010), No. 7, p. 2262.
- [2] C.T.J. Low and F.C. Walsh, Electrodeposition of tin, copper and tin-copper alloys from a methanesulfonic acid electrolyte containing a perfluorinated cationic surfactant, *Surf. Coat. Technol.*, 202(2008), No. 8, p. 1339.
- [3] Y.H. Chen, Y.Y. Wang, and C.C. Wan, Microstructural characteristics of immersion tin coatings on copper circuitries in circuit boards, *Surf. Coat. Technol.*, 202(2007), No. 3, p. 417.
- [4] Y.W. Park, T.S.N. Sankara Narayanan, and K.Y. Lee, Effect of temperature on the fretting corrosion of tin plated copper alloy contacts, *Wear*, 262(2007), No. 3-4, p. 320.
- [5] C.T.J. Low and F.C. Walsh, The stability of an acidic tin methanesulfonate electrolyte in the presence of a hydroquinone antioxidant, *Electrochim. Acta*, 53(2008), No. 16, p. 5280.

- [6] C.T.J. Low and F.C. Walsh, The influence of a perfluorinated cationic surfactant on the electrodeposition of tin from a methanesulfonic acid bath, *J. Electroanal. Chem.*, 615(2008), No. 2, p. 91.
- [7] N.M. Martyak and R. Seefeldt, Additive-effects during plating in acid tin methanesulfonate electrolytes, *Electrochim. Acta*, 49(2004), No. 25, p. 4303.
- [8] M.S. Suh, C.J. Park, and H.S. Kwon, Effects of plating parameters on alloy composition and microstructure of Sn-Bi electrodeposits from methane sulphonate bath, *Surf. Coat. Technol.*, 200(2006), No. 11, p. 3527.
- [9] M. García-Gabaldón, V. Pérez-Herranz, E. Sánchez, and S. Mestre, Effect of tin concentration on the electrical properties of ceramic membranes used as separators in electrochemical reactors, *J. Membr. Sci.*, 323(2008), No. 1, p. 213.
- [10] J.W. Wu, G.F. Zhai, Q. Chen, J.Q. Wang, and G. Ren, The interfacial structure of plated copper alloy resistance spot welded joint, *Appl. Surf. Sci.*, 254(2008), No. 22, p. 7227.
- [11] G.S. Tzeng, S.H. Lin, Y.Y. Wang, and C.C. Wan, Effects of additives on the electrodeposition of tin from an acidic Sn(II) bath, *J. Appl. Electrochem.*, 26(1996), No. 4, p. 419.
- [12] I.A. Carlos, E.D. Bidoia, E.M.J.A. Pallone, M.R.H. Almeida, and C.A.C. Souza, Effect of tartrate content on aging and deposition condition of copper-tin electrodeposits from a non-cyanide acid bath, *Surf. Coat. Technol.*, 157(2002), No. 1, p. 14.
- [13] G.P. Rockwell and J.R. Dahn, Sn-based roughness gradients for high-throughput screening, *Thin Solid Films*, 516(2008), No. 21, p. 7361.
- [14] F.X. Xiao, Y.J. Wei, F.F. Li, X.C. Zhao, and T. Liu, Influence of formaldehyde and emulsifier OP on semi-bright tin plating of printed circuit board in acidic bath, *Mater. Prot.*, 44(2011), No. 1, p. 1.
- [15] L.M. Zhang, J.L. Fang, G.W. Yuan, and P.D. Shen, *Practical Electroplating Additives*, Chemical Industry Press, Beijing, 2007, p. 468.
- [16] Crosby and N. Jeffrey, *Tin Plating*, United States Patent, 7160629, 2007.
- [17] Paul M.S. Monk, *Fundamentals of Electro-Analytical Chemistry* John Wiley & Sons, New York, 2008, p. 234.
- [18] S. Kruglikov, E. Averin, K. Simmov, and V. Kharlamov, Bright tin plating baths, [in] *National Association for Surface Finishing Annual Technical Conference*, Kentucky, 2009, p. 351.
- [19] G.I. Medvedev and N.A. Makrushin, Electrodeposition of tin from sulfate electrolyte in the presence of syntanol, formaldehyde, and allyl alcohol, *Russ. J. Appl. Chem.*, 77(2004), No. 11, p. 1781.
- [20] J.L. Fang, *Theory and Application of Electroplating Additives*, Chemical Industry Press, Beijing, 2007, p. 224.
- [21] F.X. Xiao, X.N. Shen, Y.J. Wei, and F.F. Li, Influence of gelatin and benzaldehyde on semi-bright tin coating electrodeposited in acidic bath, *Mater. Prot.*, 44(2011), No. 5, p. 1.