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# Kinetics of Sn electrodeposition from Sn(II)-citrate solutions

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## ABSTRACT

The influence of solution chemistry on the electrodeposition of Sn from Sn(II)–citrate solutions is studied. The distribution of various Sn(II)–citrate complexes and citrate ligands is calculated and the results presented as speciation diagrams. At a SnCl<sub>2</sub>·H<sub>2</sub>O concentration of 0.22 mol/L and citrate concentration from 0.30 mol/L to 0.66 mol/L, SnH<sub>3</sub>L<sup>+</sup> (where L represents the tetravalent citrate ligand) is the main species at pH below about 1.2 and SnHL<sup>-</sup> is the main species at pH above about 4. Polarization studies and reduction potential calculations show that the Sn(II)–citrate complexes have similar reduction potentials at a given solution composition and pH. However, the Sn(II)–citrate complexes become more difficult to reduce with higher total citrate concentration and higher solution pH. Nevertheless, SnHL<sup>-</sup> which forms at higher pH is a favored Sn(II)–citrate complex for Sn electrodeposition due to better plated film morphology, likely as a result of its slower electroplating kinetics. Precipitates are formed from the Sn(II)–citrate solutions after adding hydrochloric acid (to lower the pH). Compositional and structural analyses indicate that the precipitates may have the formula Sn<sub>2</sub>L.

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#### 1. Introduction

Increasing health and environmental concerns worldwide regarding the toxicity of Pb, and legislation to prohibit or restrict the use of Sn–Pb solders, have stimulated the development of different Sn-rich alloys as alternative solders in electronic assemblies [1–3]. As Sn is the main ingredient in these alloys, studies on Sn solution chemistry and, in particular, the role of complexing agents in Sn electrodeposition are beneficial.

Different complexing agents have been investigated and citrate is one of the most extensively studied ones, particularly in the electrodeposition of pure Cu [4,5] and Cu and Co alloys, such as Cu–Ni [6–8], Cu–Co [9], Co–Mo [10], and Co–W [11]. Citrate has also been used in Sn, Sn–Au, Sn–Cu, and Sn–Co electrodeposition [12–15]. Citrate has been shown to be a suitable complexing agent, because good quality Sn and Sn-rich alloys have been obtained and more importantly because of its inherent low toxicity. Moreover, citrate can function as a brightening, leveling, and buffering agent, thus eliminating the need for other plating bath additives [4,6].

The formation of Sn(II)-citrate complexes in solutions containing both stannous chloride and ammonium citrate was confirmed by Hess and Taft [16] in 1938 from the observation that the addition of sodium carbonate to the solution did not result in any precipitation. A kinetic model for Sn electrodeposition from citrate solutions was proposed by Survila et al. [17] for the codeposition of Sn and Co.  $SnL^{2-}$  and  $SnHL^{-}$  (where L represents the tetravalent citrate ligand and citric acid can be represented as H<sub>4</sub>L) were considered as the most likely complexes formed in acidic solutions. A stability constant of  $3.2\times10^{19}$  for SnHL- was determined experimentally by Survila et al. [17]. Their distribution diagrams of Sn(II)-citrate complexes showed that at a  $Sn^{2+}$ concentration of 0.05 mol/L and a citrate concentration of either 0.1 mol/L or 0.3 mol/L, SnHL<sup>-</sup> was the main species between pH 2 and 4,  $SnL^{2-}$  was the main species at pH>4 and  $Sn^{2+}$  was the dominant species below pH 2. Although several other researchers have also studied the Sn(II)-citrate system [18-21], there are differences among the proposed stability constants and distributions for Sn(II)-citrate complexes. Jean and Sinicki [19] proposed three mono-nuclear complexes, SnH<sub>3</sub>L<sup>+</sup>, SnH<sub>2</sub>L, and SnHL<sup>-</sup>, and calculated their stability constants, which were  $3.2 \times 10^5$ ,  $2.5 \times 10^7$ , and  $2.0 \times 10^{10}$ , respectively. Tikhonov and Kurolap [20] used potentiometric methods to study the complexes formed between citric acids and stannous ions and showed that SnHL<sup>-</sup> formed when the pH was below 7 and  $SnH(OH)L^{2-}$  formed when the pH was greater than or equal to 7. Elbourne and Buchanan [21] proposed the formation of two different Sn(II)-citrate complexes in solutions containing 0.4 mol/L citrate and different concentrations of stannous ions. They proposed that in a solution containing  $1 \times 10^{-3}$  mol/L to  $2 \times 10^{-3}$  mol/L stannous ions a bi-nuclear structure (Sn<sub>2</sub>(H<sub>2</sub>L)<sub>2</sub>) was formed, where two citrate groups chelated with two stannous ions.





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However, in solutions containing higher concentrations of stannous ions  $(2.5 \times 10^{-3} \text{ mol/L})$ , a mono-nuclear structure  $(\text{Sn}(\text{C}_6\text{H}_6\text{O}_6)_2)$  was formed, where two citrate groups chelated with one stannous ion. The stability constants for the complexes were not determined.

One concern about a citrate electroplating solution is its instability. Although precipitation has occurred in the Sn(II)-citrate solution, the precipitates have never been characterized. The principal objective of this investigation was to study Sn(II)-citrate solution chemistry, to study the reduction behavior of Sn(II) from the Sn(II)-citrate solution and to identify precipitates formed in the Sn(II)-citrate solutions to better understand the kinetics of Sn electrodeposition from Sn(II)-citrate solutions.

## 2. Experimental

## 2.1. Solution preparation

The Sn(II)-citrate solutions were prepared by dissolving triammonium citrate in deionized water, followed by the dissolution of SnCl<sub>2</sub>·2H<sub>2</sub>O in the citrate solution. The deionized water was obtained from an Aqua MAXTM-ultra purification system. Solution pH was adjusted by the addition of HCl.

## 2.2. Identification of precipitates

Precipitates were formed in the Sn(II)–citrate solutions when the pH was decreased. The precipitates were analyzed using wide angle X-ray diffraction (XRD) with a Rigaku rotating Co anode system, operating in continuous scanning mode at a voltage of 40 kV and a current of 160 mA. X-ray photoelectron spectroscopy (XPS) was also performed on samples using an AXIS-165 XPS system with an Al K $\alpha$  (1400 eV) X-ray source with a resolution of 0.5 eV. The binding energies of the C 1s, O 1s, and Sn 3d<sub>5/2</sub> levels were detected and the C 1s (284.65 eV) level was taken as the standard for calibration. Atomic ratios of carbon to oxygen, carbon to tin and oxygen to tin (C/O, C/S, O/Sn) were determined from fits to the survey spectra. Citric acid and tri-ammonium citrate were used as reference specimens.

## 2.3. Polarization measurements

Polarization measurements were performed using a Gamry electrochemical system operating at a scanning rate of 1 mV/s. Platinum was used as both the working and the counter electrodes, and a saturated calomel electrode (SCE) was used as the reference electrode.

#### 2.4. Electrodeposition experiments

All electrodeposition was done on Si wafer pieces, metallized with a 25-nm Ti adhesion layer and a 200-nm Au seed layer. A Dynatronix DuPR 10-0.1-0.3 pulse plating power supply was used for electrodeposition, with a 2-ms forward on-time and 8-ms forward off-time. All electrodeposition was done with a current density of 5 mA/cm<sup>2</sup> at room temperature for 30 min. The microstructure and composition of the Sn films plated under different conditions were characterized using a Hitachi H2700 scanning electron microscope (SEM), equipped with an ultra thin window energy dispersive X-ray (EDX) spectrometer.

## 3. Results and discussion

In order to determine the distribution of various Sn(II)-citrate species in solution, it is necessary to know their stability constants.

#### Table 1

Stability constants for Sn(II)-citrate complex ions and Sn(II)-hydroxyl species ("L" represents tetravalent citrate ligands)

Equilibrium	log K	Ref.
$\mathrm{H^{+}+HL^{3-}\rightarrow H_{2}L^{2-}}$	5.69	[22]
$\mathrm{H^{+}} + \mathrm{H_{2}}\mathrm{L^{2-}} \rightarrow \mathrm{H_{3}}\mathrm{L^{-}}$	4.35	[22]
$\mathrm{H}^{+} + \mathrm{H}_{3}\mathrm{L}^{-} \to \mathrm{H}_{4}\mathrm{L}$	2.87	[22]
$\mathrm{Sn}^{2+} + \mathrm{HL}^{3-} \rightarrow \mathrm{Sn}\mathrm{HL}^{-}$	19.5	[17]
	10.3	[18,19]
$Sn^{2+} + H_2L^{2-} \rightarrow SnH_2L$	7.4	[18,19]
$Sn^{2+} + H_3L^- \rightarrow SnH_3L^+$	5.5	[18,19]
$Sn^{2+} + H_2O \rightarrow SnOH^+ + H^+$	-3.8	[23]
$Sn^{2+} + H_2O \rightarrow Sn(OH)_2 + H^+$	-7.8	[23]
$\operatorname{Sn}^{2+} + \operatorname{H}_2 O \rightarrow \operatorname{Sn}(OH)_3^- + H^+$	-17.5	[23]
$Sn^{2+} + H_2O \rightarrow Sn_2(OH)_2^{2+} + (H^+)^2$	-2.4	[23]
$Sn^{2+} + H_2O \rightarrow Sn_2(OH)_3^+ + H^+$	-6.66	[23]
$Sn^{2+} + H_2O \rightarrow Sn_3(OH)_4^{2+} + H^+$	-5.6	[23]

### Table 2

Selected free energy data for the Sn(II)-citrate system at 298 K

Species	$\Delta G_{\mathrm{f}^{\circ}}$ (kJ/mol)	Ref.
Citric acid (H <sub>4</sub> L)	-1236.4	[24]
H+ (aq.)	0	[24]
Sn <sup>2+</sup> (aq.)	-27.2	[24]
Sn (white)	0	[24]

Two different sets of stability constants for SnHL<sup>–</sup> were found in the literature, as shown in Table 1. To determine which stability constants were applicable to the solutions in this work, calculations with data from both the literature and experiments were done and are described below.

From the stability constants for citric acid (Table 1), the following data can be obtained:

$$3H^+ + HL^{3-} \rightarrow H_4L \quad K = 10^{12.9}$$
 (1)

$$\Delta G^{\circ} = -RT \ln K = \Delta G^{\circ}_{f,H_4L} - \Delta G^{\circ}_{f,HL^{3-}} - 3\Delta G^{\circ}_{f,H^+}$$

From the above equations and the free energy data in Table 2, the standard Gibbs free energy of formation for  $HL^{3-}$  can be calculated as -1162.81 k]/mol.

Speciation calculations were initially performed on a solution containing 0.22 mol/L SnCl<sub>2</sub> and 0.30 mol/L tri-ammonium citrate, which is labeled as S1 (Table 3). This particular solution was chosen because 0.30 mol/L of tri-ammonium citrate has been shown to be the minimum amount required to completely dissolve 0.22 mol/L SnCl<sub>2</sub> [25]. The natural pH of solution S1 is 4.1. At this pH, all three ammonium ions should fully dissociate from the citrate ions and each citrate ion can carry up to four protons, thus forming H<sub>4</sub>L, H<sub>3</sub>L<sup>-</sup>, H<sub>2</sub>L<sup>2-</sup> and HL<sup>3-</sup>. Only H<sub>3</sub>L<sup>-</sup>, H<sub>2</sub>L<sup>2-</sup> and HL<sup>3-</sup> are considered as ligand species with Sn<sup>2+</sup> ions in solution. Survila et al. [17] considered both SnHL<sup>-</sup> and SnL<sup>2-</sup> in their model for Sn(II)-citrate complexes. The difference is that they used citric acid instead of tri-ammonium citrate. One important consideration for tri-ammonium citrate is that the proton in the ternary hydroxyl group is difficult to dissociate at a pH of 4.1, so that SnHL<sup>-</sup> was more likely to form in solution S1. To simplify the calculation, all Sn<sup>2+</sup> ions were assumed to form SnHL<sup>-</sup> complexes with the citrate, so that the

Table 3		
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Composition of Sn-citrate solutions used in this study

	S1	S2	S3	S4
SnCl <sub>2</sub> ·2H <sub>2</sub> O (mol/L)	0.22	0.22	0.22	0.22
Tri-ammonium citrate (mol/L)	0.30	0.33	0.44	0.66



SC

tion of SnCl\_2  $\cdot$  2H<sub>2</sub>O was kept at 0.22 mol/L, while the concentration of tri-ammonium citrate was varied as follows: S1, 0.30 mol/L; S2, 0.33 mol/L; S3, 0.44 mol/L; S4, 0.66 mol/L.

concentration of SnHL<sup>-</sup> would be 0.22 mol/L and the concentration of HL<sup>3-</sup> would be 0.08 mol/L. From the polarization measurements shown in Fig. 1, the reduction of SnHL<sup>-</sup> started at about -0.64 V versus SCE (i.e., -0.398 V versus NHE). A further decrease in applied potential caused an almost linear increase in the current density, until at about -0.75 V, where a plateau appeared which is the limiting current density for SnHL<sup>-</sup> reduction in solution S1.

The reduction reaction for SnHL- during the electrodeposition of Sn can be given as:

$$SnHL^{-} + 2e \rightarrow Sn + HL^{3-}$$
(2)

A potential of -0.398 V versus NHE, from the polarization measurements, was used as the reduction potential for reaction (2) in the following calculation. It follows from the Nernst equation that:

$$E = E^{\circ} + \frac{RT}{nF} \ln \frac{[\text{SnHL}^-]}{[\text{HL}^{3-}]} = -0.398 \text{ V versus NHE}$$

The standard electrode potential  $E^{\circ}$  for reaction (2) can be calculated as -0.41 V versus NHE. The standard Gibbs free energy change for this reaction is equal to:

$$\Delta G^{\circ} = -nFE^{\circ} = \Delta G^{\circ}_{f, \text{HL}^{3-}} + \Delta G^{\circ}_{f, \text{Sn}} - \Delta G^{\circ}_{f, \text{SnHL}^{-}} = 79.3 \text{ kJ/mol}$$

From the above equations and data shown in Table 2, the standard Gibbs free energy of formation for SnHL<sup>-</sup> is -1242.11 kJ/mol.

The SnHL<sup>-</sup> complex forms according to:

$$\mathrm{Sn}^{2+} + \mathrm{HL}^{3-} \to \mathrm{Sn}\mathrm{HL}^{-} \tag{3}$$

The standard Gibbs free energy change for the formation of SnHL<sup>-</sup> is:

$$\Delta G^{\circ} = -RT \ln K = \Delta G^{\circ}_{f, \text{SnHL}^-} - \Delta G^{\circ}_{f, \text{HL}^{3-}} - \Delta G^{\circ}_{f, \text{Sn}^{2+}}$$
  
Thus:

$$K = e^{\Delta G^{\circ}/-RT} = 1.36 \times 10^9$$
 and  $\log K = 9.1$ 

Comparing this value with the data from the literature, the stability constant for SnHL<sup>-</sup> from [18,19] (i.e.,  $\log K = 10.3$ ) is much closer to our results and thus was used in the subsequent calculations.

Other than the formation of Sn(II)–citrate complexes, Sn<sup>2+</sup> ion hydrolysis was also taken into account and the available stability constants are listed in Table 1. In this study, the equilibrium concentrations of the citrate complexes and all other compounds were



Fig. 2. Sn(II)-citrate speciation diagram as a function of pH for solution S1 (0.22 mol/L Sn<sup>2+</sup> and 0.30 mol/L tri-ammonium citrate).  $\gamma$  is the molar fraction of Sn(II)-citrate complexes.

calculated with the aid of spreadsheet software (e.g., Microsoft Excel). To perform a calculation, the concentrations of all possible Sn(II)-citrate complexes and Sn<sup>2+</sup> hydrolysis products were expressed as a function of the concentration of SnHL<sup>-</sup>, Sn<sup>2+</sup> and/or the pH of the solution, respectively. Then, mass balance equations for both Sn and citrate were set up, so that the concentration of SnHL<sup>-</sup> could be calculated at a given pH. Subsequently, the concentrations of all the other species were calculated.

The two mass balance equations used during the calculations are:

$$C_{citrate} = [H_4L] + [H_3L^-] + [H_2L^{2-}] + [HL^{3-}] + [SnH_3L^+] + [SnH_2L] + [SnHL^-]$$
(4)

$$C_{Sn(II)} = [SnH_3L^+] + [SnH_2L] + [SnHL^-] + [Sn^{2+}] + [SnOH^+] + [Sn(OH)_2] + [Sn(OH)_3^-] + 2[Sn_2(OH)_2^{2+}] + 2[Sn_2(OH)_3^+] + 3[Sn_3(OH)_4^{2+}]$$
(5)

The distribution of Sn(II)-citrate complexes (SnH<sub>3</sub>L<sup>+</sup>, SnH<sub>2</sub>L, and SnHL<sup>-</sup>), in molar fraction as a function of pH for solution S1, is shown in Fig. 2. The concentration of Sn<sup>2+</sup> ions is in the range of 10<sup>-3</sup> mol/L to 10<sup>-9</sup> mol/L and concentrations of all the Sn<sup>2+</sup> hydrolysis products shown in Eq. (5) are in the range of  $10^{-5}$  mol/L to  $10^{-40}$  mol/L and are not shown in the distribution diagram. It can be noted that at the solution natural pH of 4.1, the main species in solution S1 is SnHL<sup>-</sup>, with a very small amount of SnH<sub>2</sub>L. This result may explain the observation that when S1 is stored in a sealed bottle for 2 months, a small amount of precipitates appears and settles to the bottom of the container. Assuming the precipitates are in fact SnH<sub>2</sub>L, S1 should not be stable in the pH region where the SnH<sub>2</sub>L concentration is high enough to precipitate out.

Hydrochloric acid was added to solution S1 to decrease the pH. During the pH adjustment, the solution remained clear until the pH reached about 3.3. When the pH was decreased to about 3.1, a small amount of precipitates started forming. Once the solution was stirred for about 30 s, more precipitates formed, and eventually solution S1 became milky in appearance, with white precipitates settling on the bottom of the container. During precipitation, the solution pH increased to about 3.3 and remained at that value.

-0.016

-0.014

-0.012

-0.010 j / A cm<sup>-2</sup>

-0.006

-0.004

-0.002

When the pH was lowered to 2.5, more precipitates formed; this was likely due to the formation of more  $SnH_2L$  based on Fig. 2. As more HCl was added, the precipitates started to dissolve and the solution became almost clear at a pH of 1.1. This disappearance of precipitates can be explained by the dissolution of  $SnH_2L$  and the formation of  $SnH_3L^+$  as the main Sn(II)-citrate complex (Fig. 2).

The same calculations were carried out for solutions S2, S3, and S4 (Table 3). For solutions S1, S2, S3, and S4, the concentration of SnCl<sub>2</sub>·2H<sub>2</sub>O was fixed at 0.22 mol/L, while the concentration of tri-ammonium citrate was varied from 0.30 mol/L to 0.66 mol/L. The concentrations of Sn(II)-citrate complexes (SnH<sub>3</sub>L<sup>+</sup>, SnH<sub>2</sub>L, and SnHL<sup>-</sup>) and citrate species (H<sub>4</sub>L, H<sub>3</sub>L<sup>-</sup>,  $H_2L^{2-}$ , and  $HL^{3-}$ ) as a function of pH are shown in Fig. 3a-d. There is almost no change in the distribution of the different Sn(II)-citrate complexes as the concentration of tri-ammonium citrate is increased from 0.30 mol/L to 0.66 mol/L. but the distribution of the citrate species changes. The peak positions of the curves for these four citrate species staved the same for S1, S2, S3, and S4, but the height of each peak increased with increasing tri-ammonium citrate concentration. The standard electrode potentials ( $E^{\circ}$ ) for the reduction of Sn(II) to Sn<sup>0</sup> from SnHL<sup>-</sup>, SnH<sub>2</sub>L, and SnH<sub>3</sub>L<sup>+</sup>, calculated from Gibbs free energy data, were -0.69 V, -0.60 V, and -0.54 V versus SCE, respectively. These results show that SnH<sub>3</sub>L<sup>+</sup> is the easiest to reduce, followed by SnH<sub>2</sub>L and then SnHL<sup>-</sup>. To find out the effect of citrate species distribution on the reduction behavior of the Sn(II)-complexes, the reduction potentials (E) for SnHL<sup>-</sup>, SnH<sub>2</sub>L, and SnH<sub>3</sub>L<sup>+</sup> were calculated using the Nernst equation for solutions S1, S2, S3, and S4 and the results are shown in Fig. 4a. In each solution, the reduction potentials for the three Sn(II)-citrate complexes were similar, although there is a slight increase from SnHL<sup>-</sup> to SnH<sub>2</sub>L and from SnH<sub>2</sub>L to SnH<sub>3</sub>L<sup>+</sup>. In addition, as the concentration of tri-ammonium citrate was increased from 0.30 mol/L to 0.66 mol/L, the reduction potentials for the Sn(II)-citrate complexes decreased from -0.61 V to about -0.68 V versus SCE. The calculated and experimental reduction potentials are shown in Fig. 4b; both follow the same trend. The values for each Sn(II)-citrate complex are so close that they overlap one another and thus only one data point is shown for each solution. The reduction potentials from the polarization measurements were more negative than the calculated values, because during the polarization measurements, in addition to the overpotential needed to support the electrochemical reactions, the applied potential also must cover the ohmic drop required to drive the ionic current in solution. Since the reduction potential for all three Sn(II)-citrate complexes were very close to one another, it is also quite possible that they would participate in the reduction reaction at the same time, and be reduced to Sn metal on the cathode.

The same calculations for reduction potentials were also carried out for solution S1, with different pH values, and the results are shown in Fig. 5a. The pH was adjusted in the same way as before. At each pH value, the reduction potentials for SnHL<sup>-</sup>, SnH<sub>2</sub>L, and SnH<sub>3</sub>L<sup>+</sup> were again similar to one another, with a very slight increase from SnHL<sup>-</sup> to SnH<sub>2</sub>L and then to SnH<sub>3</sub>L<sup>+</sup>. As the pH was



Fig. 3. Speciation diagrams as a function of pH for solutions S1 (a), S2 (b), S3 (c), and S4 (d). Note that all solutions contain 0.22 mol/L Sn<sup>2+</sup>, but different concentrations of tri-ammonium citrate: 0.30 mol/L (a), 0.33 mol/L (b), 0.44 mol/L (c), and 0.66 mol/L (d).



**Fig. 4.** (a) Calculated reduction potentials for SnHL<sup>-</sup>, SnH<sub>2</sub>L, and SnH<sub>3</sub>L<sup>+</sup> for solutions S1, S2, S3, and S4 at natural pH. (b) A comparison of calculated and experimental reduction potentials as a function of tri-ammonium citrate concentration.

decreased from 4.1 to 2.5 and then to 1.1, the reduction potentials became less negative, moving from -0.615 V to -0.53 V and then to -0.48 V versus SCE, which means that the Sn(II)-citrate complexes became easier to reduce at lower pH.

To help explain the above calculations, polarization measurements were performed for solution S1 with pH values of 1.1, 2.5, and 4.1, and the results are shown in Fig. 5b. The reduction potential change as a function of pH showed a similar trend to the calculated



**Fig. 5.** (a) Calculated reduction potentials for SnHL<sup>-</sup>, SnH<sub>2</sub>L, and SnH<sub>3</sub>L<sup>+</sup> for solution S1 (0.22 mol/L Sn<sup>2+</sup> and 0.30 mol/L tri-ammonium citrate) at pH 1.1, 2.5, and 4.1. (b) Polarization curves for solution S1 at pH 1.1, 2.5, and 4.1. (c) A comparison of calculated and experimental reduction potentials for solution S1 as a function of pH.

results. The current density for solution S1, with a pH of 2.5, was very low, lower than the values for the other two solutions. This is due to the formation of a significant quantity of precipitates at a pH value of 2.5. In addition, both the Sn and citrate concentrations in the solution were much lower. The polarization curve for solution S1, with a pH of 1.1, showed an almost linear dependence, due to significant hydrogen evolution at this pH. By comparison, the calculated and experimental reduction potentials for different pH values are combined in Fig. 5c. The data follow the same trend, with the measured reduction potential being more negative for the reasons stated previously.

Electrodeposition of Sn from solution S1, with pH values of 1.1, 2.5, and 4.1, was carried out on Au-coated Si substrates. SEM secondary electron (SE) images for both plan views and cross-sections of the as-deposited Sn films are shown in Fig. 6a–c. The magnification for Fig. 6a is 5 times lower than that for Fig. 6b and c. EDX point analysis at the positions identified in the plan views of Fig. 6a and b is shown in Fig. 7a and b. EDX spectra from point 1 (the smooth

area) and point 2 (one of the large particles) in Fig. 6a are shown in Fig. 7a-1 and a-2. The EDX spectrum in Fig. 7a-1 is mostly Au with a small Sn peak. The Au is from the underlying seed layer and the Sn is from a thin continuous Sn layer ( $\ll 1 \mu m$  thick), which forms during the initial nucleation stage from the reduction of SnH<sub>3</sub>L<sup>+</sup>, SnH<sub>2</sub>L, and SnHL<sup>-</sup>. The larger particles are pure Sn (Fig. 7a-2). At a pH of 2.5, a thicker continuous Sn layer (about 0.8 µm thick) forms before isolated Sn particles grow preferentially (Fig. 7b-1 and b-2). The reason why the continuous Sn layer is thicker at pH 2.5 than at pH 1.1 is that the concentration of SnHL<sup>-</sup> is much higher at pH 2.5 than at pH 1.1. This is important because SnHL<sup>-</sup> has a slower plating rate and is more likely to form a continuous layer. Consequently, fewer and smaller Sn particles are formed at this pH. At the natural pH (solution S1), a dense Sn film forms with a thickness of about 5 µm. All three cross-section samples were prepared by cleaving with a diamond scribe, and the cross-section image in Fig. 6c is not perfectly edge-on, so some of the surface is visible.



Fig. 6. SEM secondary electron (SE) images (plan view and cross-section) of Sn films electrodeposited from solution S1 (0.22 mol/L Sn<sup>2+</sup> and 0.30 mol/L tri-ammonium citrate) at pH 1.1 (a), 2.5 (b), and 4.1 (c).



**Fig. 7.** EDX point analysis for Sn plated from solution S1 at pH 1.1 (a-1 and a-2) and 2.5 (b-1 and b-2).

As shown in Fig. 2, at a pH of 1.1, the main complex in the solution is  $SnH_3L^+$ . With a positive charge,  $SnH_3L^+$  will be easily attracted to cathode. In addition, as shown in Fig. 5a,  $SnH_3L^+$  becomes easier to reduce at pH 1.1 than at higher pH values. All these contribute to the high growth rate of Sn on the cathode. In contrast to  $SnH_3L^+$ , the  $SnHL^-$  species (which forms at higher pH values) has a negative charge. The charge distribution within the polar complex ions must be aligned to facilitate attraction to the cathode, so that mass transfer will be slower and the deposited film should have sufficient time to densify.

XRD and XPS were used in an attempt to identify the precipitates from solution S1, which formed at different pH values, and precipitates from solution S2, S3, and S4 when the pH was decreased. XRD and XPS analyses indicated that the precipitates had the same structure and composition. An XRD pattern, from precipitates which had formed from solution S1 at a pH of 2.5, is shown in Fig. 8. The pattern is quite complex, with the strongest peak at  $2\theta = 11.75^{\circ}$ . The pattern does not match XRD patterns obtained for tri-ammonium citrate, citric acid, tin chloride dihydrate or tin oxide. We were unable to index the pattern.



Fig. 8. XRD pattern for precipitates obtained from solution S1 at pH 2.5.

Fig. 9 shows an XPS survey spectrum for the precipitates from solution S1 (pH 2.5). Several elements, including Sn, C, O, Cl, and N were detected. There was a small amount of N (about 0.7 at.%) and Cl (about 0.5 at.%) present in the precipitates. XPS analysis was done on standard citric acid and tri-ammonium citrate samples for comparison. Similar N levels (about 0.2 at.%) were detected in the citric acid specimen and similar Cl levels (about 0.3 at.%) were detected in the tri-ammonium citrate specimen, and may be due to contamination.

Fig. 10 shows the C 1s XPS spectra for citric acid, tri-ammonium citrate and the Sn(II)–citrate solution precipitates. Three peaks were identified by peak fitting and these correspond to different surroundings for carbon, which match the number of C bond types in both citric acid and tri-ammonium citrate. The C 1s peaks at 284.65 eV (Table 4) are assigned to methyl carbons [18,26,27], while the peaks at 286.4 eV (citric acid), 286.53 eV (tri-ammonium citrate), and 286.27 eV (Sn(II)–citrate precipitates) correspond to carbon bonded to carbonyl groups [18,27]. The peaks at 288.78 eV (citric acid), 288.65 eV (tri-ammonium citrate) and 288.36 eV (Sn(II)–citrate precipitates) are attributed to carbon atoms of COO– groups, which is also in agreement with the binding energy values reported for acetyl carbons [18,26–28].

Fig. 11 shows the O 1s XPS spectra for citric acid, tri-ammonium citrate and Sn(II)–citrate precipitates. Two peaks were deconvoluted for both citric acid and tri-ammonium citrate, and these also matched the number of O bonds in both reference specimens. The high binding energy for O 1s at 533.07 eV (citric acid) and 533.03 eV (tri-ammonium citrate) can be assigned to oxygen atoms in –C–OH [27,29] groups and the oxygen peaks at 531.84 eV (citric acid) and 531.77 eV (tri-ammonium citrate) can be assigned to –COO<sup>–</sup> groups



Fig. 9. XPS survey spectrum for precipitates obtained from solution S1 at pH 2.5.

## Table 4

Binding energy for main components of XPS C 1s, O 1s, and Sn 3d<sub>5/2</sub> peaks for citric acid, tri-ammonium citrate, and precipitates obtained from solution S1 at pH 2.5 (peak indexing was made with reference to Refs. [18,26–32])

Binding energy (eV)							
IPS peak parameters C 1s			O 1s			Sn 3d <sub>5/2</sub>	
Components		—с—он	—coo	—соом	—соон	С—О—Н	0—Sn—O
Citric acid	284.65	286.49	288.78		531.84	533.07	
Tri-ammonium citrate	284.65	286.53	288.65	531.77		533.03	
Sn-citrate precipitate	284.65	286.27	288.36	531.47			486.8



**Fig. 10.** XPS C 1s spectrum from: (a) citric acid, (b) tri-ammonium citrate, and (c) precipitates obtained from solution S1 at pH 2.5.

[26–29]. It should be noted that the binding energies for O 1s in –COOH (531.84 eV) and –COO–M (531.77 eV) are very close. For the Sn(II)–citrate precipitates, the O 1s spectrum has only one peak with a binding energy of 531.47 eV, suggesting equivalent oxygen atoms and implying equivalency of the two Sn atoms to which they are bound. Comparison with the reference O 1s peaks in citric acid and tri-ammonium citrate indicates that the O 1s peak for the precipitates is associated with –COOH bonds and/or –COO–M bonds, with no C–O–H bonds. The O 1s binding energy for the Sn(II)–citrate precipitates was lower than that for citric acid and tri-ammonium citrate by 0.37 eV and 0.3 eV, respectively, which can



**Fig. 11.** XPS O 1s spectrum from: (a) citric acid, (b) tri-ammonium citrate, and (c) precipitates obtained from solution S1 at pH 2.5.

be attributed to a decrease in the electron density of the carboxyl oxygen by an increase in the positive environment produced by Sn(II). Two other Sn(II)–citrate precipitates that formed in solution S1, with a pH of 2.5, produced similar XPS spectra.

The XPS Sn 3d core level spectrum, with a binding energy of 486.8 eV, from the precipitates is shown in Fig. 12. It is difficult to distinguish between O-Sn(II)-O and O-Sn(IV)-O since the positions of the Sn  $3d_{5/2}$  peaks for Sn(II) and Sn(IV) oxy/hydroxy compounds partially overlap:  $486.3 \pm 0.6 \text{ eV}$ (SnO) and  $486.9 \pm 0.6 \text{ eV} (SnO_2)$  [18,30–32]. Considering that triammonium citrate was not likely an oxidizing agent for stannous ions in solution, the Sn  $3d_{5/2}$  line at 486.8 eV could indicate the presence of a Sn(II) compound. Quantitative analysis, based on the area estimated from the XPS C 1s, O 1s, and Sn 3d<sub>5/2</sub> spectra, was carried out and the atomic concentrations of C and O in citric acid and tri-ammonium citrate and C, O and Sn in the Sn(II)-citrate precipitates are shown in Table 5. The relative concentrations of C/O for citric acid and tri-ammonium citrate are 1.23 and 1.11, respectively, which are higher than the ratio of 0.86 calculated from the chemical formulas of citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>) and tri-ammonium citrate ((NH<sub>4</sub>)<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>). This indicates that some C contamination from air occurred and the calculated C concentrations are too high. The same effect would be expected for Sn(II)-citrate precipitates under the same working conditions, giving higher C/Sn relative concentrations than expected. Therefore, the actual C/Sn atomic ratio in the Sn(II)-citrate precipitates is lower than 3.86, e.g., 3, 2 or 1. Taking into account that there are no C-O-H bonds for the O 1s spectrum for the precipitate (Fig. 11), the Sn<sub>2</sub>L structure shown in Fig. 13 is proposed, with a C/Sn atomic ratio of 3. Each citrate molecule is combined with four stannous ions through O bonds, and connected with another four citrates. Each stannous ion is connected with two citrates through O bonds.



**Fig. 12.** XPS Sn 3d core level spectrum for precipitates obtained from solution S1 at pH 2.5. The thick solid line is the experimental spectrum; the thin line is the fitted spectrum.

Table 5		
Composition results for citric acid, tri-amr	monium citrate and precipitates obtained	d from solution S1 at pH 2.5

Element Atom concentration (%)			Atomic ratio		Atomic ratio		
	С	0	Sn	C/O (theoretical)	C/O (actual)	C/Sn	O/Sn
Citric acid	55.0	44.8		0.86	1.2		
Tri-ammonium citrate	51.1	46.1		0.86	1.1		
Sn-citrate precipitate	46.5	40.2	12.0	0.86	1.2	3.9	3.3



**Fig. 13.** Structure of Sn(II)-citrate precipitate with a formula of  $Sn_2L$  (where L represents the tetravalent citrate ligand).

Thermodynamic calculations, based on the SnHL<sup>-</sup>, SnH<sub>2</sub>L, and SnH<sub>3</sub>L<sup>+</sup> stability constants proposed by Jean and Sinicki [19], match the polarization measurements and electrodeposition experiments very well. In addition, precipitate formation from the Sn(II)–citrate solutions followed the predicted complex distribution diagrams as well. It is possible that the Sn(II)–citrate neutral molecule is Sn<sub>2</sub>L and not SnH<sub>2</sub>L based on an analysis of the XPS spectra obtained. The consumption of H<sup>+</sup> during precipitation is probably due to other side reactions.

## 4. Conclusions

The distribution of Sn(II)-citrate complexes presented in this paper are useful for explaining the kinetics of Sn electrodeposition and the formation of precipitates in the citrate solutions. The distribution of Sn(II)-citrate complexes changed with solution pH, with  $SnH_3L^+$  as the main complex when the pH was lower than about 1.2 and SnHL<sup>-</sup> as the main complex when the pH was higher than about 4. The distribution of Sn(II)-citrate complexes did not change as the tri-ammonium citrate concentration was changed, while the distribution of citrate species changed. The reduction potentials for the Sn(II)-citrate complexes were almost the same at a given solution composition and pH, so that reduction of all these species likely occur simultaneously. The Sn(II)-citrate complexes were more difficult to reduce at higher tri-ammonium citrate concentrations, and were easier to reduce at lower solution pH. The SnHL<sup>-</sup> species is favored for Sn plating due to its slower electroplating kinetics which results in smoother films. The precipitates that formed in the Sn(II)-citrate solutions at low pH are proposed to be Sn<sub>2</sub>L.

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