



# Influence of current density on surface morphology and properties of pulse plated tin films from citrate electrolyte



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## ABSTRACT

Bulk polycrystalline tin films have been processed by pulse electrodeposition technique from a simple solution containing triammonium citrate and stannous chloride. The cathodic investigations have been carried out by galvanostatic methods. As deposited samples are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). XRD analysis of the deposited films shows microcrystalline grains having  $\beta$ -Sn form. The surface morphology is very rough at lower current density, but becomes smooth at higher current density, and exhibits pyramid type morphology at all the current densities. The effect of current density on microhardness, melting behavior, and electrical resistivity are also reported here.

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## 1. Introduction

Tin plating is the choice of electronic manufacturers because of its noble properties like attractive appearance, high corrosion resistance, and solderability. Generally two types of aqueous electrolytes, i.e., acidic stannous sulfate and alkaline sodium stannate based electrolytes are used for tin plating [1–4]. Investigators have also tried methane sulfonic acid, pyrophosphate, citric acid, fluoroborate, etc. based electrolytes in the past [5–8]. Most of these electrolytes are strongly acidic or alkaline, and have severe effects on environment and human health. These are corrosive in nature, cause water drainage problem, and are also environmentally hazardous. Moreover, their use is limited in microelectronic packaging because of their very low (<1) or very high (~14) pH [9]. Therefore, there is a need to have a plating bath that is more nature friendly for tin electrodeposition.

Tin plating bath based on citric acid or its salt is now being employed as a better alternative. Citrate baths have been already used for the electrodeposition of metals such as, Cu, Ni, Co and its alloys [10–13]. Citric acid and citrate are the chemicals that are used as a brightening agent, bath stabilizer and buffering agent for metal electrodeposition [7,14,15]. Generally, there is no additional requirement of organic additives in this electrolyte. Citrate ions in the citrate electrolyte react with tin ions to form tin-citrate complexes that are adsorbed on the cathode and inhibit

hydrogen evolution reaction [16]. Moreover, the bath pH is weakly acidic (>3), thus a strict control of the pH is not necessary and can be easily applied to microelectronic industries. Many investigations have been conducted to develop lead free solder alloys such as Sn–Cu, Sn–Ag, Sn–Ag–Cu, Au–Sn, Sn–Zn, Sn–Zn–Mo from citrate baths [17–23]. Recently, Sharma et al. have developed a composite solder using a citrate – stannous chloride solution by electrodeposition method [24]. However, limited research has been conducted on effect of deposition parameters on surface morphology and microstructural properties of deposited films from citrate baths.

In this work tin films have been electroplated on stainless steel substrate by pulse electrodeposition method using citrate electrolyte. This electrolyte has been selected from the previous research by the authors [24]. The citrate bath is transparent, clear solution, non toxic, non corrosive and environmental friendly. The as prepared bath pH (~4.3) is safe. There is no undissolved residue or sludge formation as compared to alkaline and acidic baths. This shows a reduced tendency toward stannic tin formation, i.e., oxidation of  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$  ions in solution. The surface morphology, and mechanical, electrical, and thermal properties of the tin films have also been evaluated.

## 2. Experimental details

### 2.1. Tin plating bath

The chemical compositions used in the present study comprise of reagent grade tin (II) chloride,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (50 g/L) and

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**Table 1**  
Pulse parameters for electrodeposition.

Parameter	Values
Current density	0.05–0.4 A/cm <sup>2</sup>
$T_{on}^a$	0.001 s
$T_{off}^b$	0.01 s
Duty cycle	9%
Pulse frequency	90 Hz
Duration <sup>c</sup>	0.8 h
Agitation	300 rpm
Bath temperature	~28 °C

Current density shown here are peak current densities.

<sup>a</sup> Time during current flows.

<sup>b</sup> Time during no current flows.

<sup>c</sup> Duration is in hours, h.

tri-ammonium citrate, C<sub>6</sub>H<sub>17</sub>N<sub>3</sub>O<sub>7</sub> (TAC) (100 g/L). The plating bath is prepared by dissolving tri-ammonium citrate in deionized water followed by the gradual addition of SnCl<sub>2</sub>·2H<sub>2</sub>O. The solution is then stirred until the stannous chloride is dissolved completely. The plating bath is maintained at room temperature (28 °C) during the electrodeposition.

## 2.2. Electroplating cell

The electroplating cell consists of a system of two electrodes, pure tin plate (99.9% electrolytic grade) with an area of 10 cm<sup>2</sup> as the anode and stainless steel as the cathode. The stainless steel is polished metallographically and mounted in epoxy resin. The cathode surface area exposed to electrolytic bath is fixed to 6 cm<sup>2</sup>. All the electrodes are washed with distilled water and subjected to ultrasonic cleaning for 6 h to remove any grease or dirt before the experiment.

## 2.3. Electrochemical measurements

The electrochemical measurements have been conducted using Autolab PGSTAT 30 with a 10 A current booster at room temperature (28 °C). The potential values are referred to (3 M KCl) Ag/AgCl standard electrode. The cathodic potential scan rate selected for polarization measurements is 1 mV/s. The pulse parameters (i.e., pulse on/off time, frequency, etc.) are based on the previous investigation on tin electroplating [24]. It is already known that to achieve a compact and uniform cathode coverage, pulse on time must be lesser than pulse off time. The pores/bubble formation in pulse plated coatings is usually minimized at lower duty cycles [26,27]. Therefore, after a series of experiments, the duty cycle is restricted to 9% with a frequency of 90 Hz. The electrodeposition parameters are shown in Table 1. The thickness of the electrodeposited films is determined by the surface profilometer (Veeco DEKTAK). A Sartorius weighing balance (CPA225D) with an accuracy of 0.01 mg is used for measuring the weight of the film.

## 2.4. Characterization studies

### 2.4.1. XRD

Pulse electrodeposited films are analyzed using an X-ray diffractometer (Bruker's D8 Advance) with Cu K $\alpha$  radiation operating at 40 kV and 30 mA current. The phases formed are identified by the comparison of the recorded diffraction peaks with the standard ICDD database using Philips X'Pert HighScore software.

### 2.4.2. SEM

The morphology evolution and grain size in the electrodeposited coatings are analyzed using a scanning electron microscope (Carl Zeiss Supra EVO 60) coupled with an energy dispersive X-ray

spectrometer (EDS). The images are obtained in secondary electron mode at an operating voltage of 20 kV.

### 2.4.3. TEM

A transmission electron microscope (Philips Technai 2 Twin G220S) operating at 200 kV is used to characterize the electrodeposited film. The samples are prepared by twin jet electro polisher (Fishione Model 120). The twin jet electro polishing is carried out in an electrolyte containing 75% ethanol and 25% (by volume) phosphoric acid at -12 °C and 5 V. The electropolished samples are cleaned with water followed by alcohol and then stored in desiccator at room temperature for characterization.

## 2.5. Properties investigated

### 2.5.1. Microhardness

The microhardness measurements are taken by a Leica Vicker's microhardness testing machine with a load of 25 g for a dwell time of 20 s. The final microhardness values reported are the average of 10 measurements performed on different locations on the surface of the films.

### 2.5.2. Differential scanning calorimetry (DSC)

A Pyris Diamond DSC (Perkin Elmer) is used to measure the melting point of the tin films. The calorimetric investigation is carried out using alumina (Al<sub>2</sub>O<sub>3</sub>) pans in which 5 to 10 mg of the material is kept during testing. The samples are heated from 50 to 250 °C at a rate of 10 °C min<sup>-1</sup>, under a N<sub>2</sub> atmosphere with a flow rate of 50 mL min<sup>-1</sup>.

### 2.5.3. Electrical resistivity

The electrical resistivity ( $\rho$ ) of Sn films is measured using a four-point probe set up with a probe spacing ( $s$ ) of 1.5 cm. Typical size of the samples used in this measurement is 6 cm  $\times$  1 cm  $\times$  0.01 cm. A constant current from Keithley current source is passed through the sample across outer leads and corresponding voltage is measured across the inner leads using a Keithley Digital Multi-Meter (DMM 2400 series). Current ( $I$ ) is set at 1 A in this study, as tests conducted using lower range of applied current result in large variations in voltage ( $V$ ). The resistivity ( $\rho$ ) values have been calculated with the following relation:

$$\rho = 2\pi s \left( \frac{V}{I} \right)$$

Advantage of using four-point probe method is the possibility to measure the sample's resistance, without any interference from the contact resistance at the probe contacts.

## 3. Results and discussion

### 3.1. Electrochemical polarization measurements

Cathodic polarization curves recorded from the selected plating bath are shown in Fig. 1. It is observed that electrochemical reduction of Sn takes place initially at ~-0.44 V (curve a). The current density increases slightly with an increase in potential from -0.44 to -1.1 V and then at -1.1 V, it increases more sharply with more negative potential. This sharp increase in current density with potential is due to the rapid evolution of hydrogen gas beyond -1.1 V. A very short plateau region exists in this case (curve a). The deposition potential increases from -0.44 to -0.63 V, i.e., it becomes more negative after the addition of TAC (curve b). This may be due to the more stability of the citrate complex. A number of citrate complexes are found in tin-citrate solutions, such as SnHL<sup>-</sup>, SnL<sup>2-</sup>, SnH<sub>3</sub>L<sup>+</sup>, SnH<sub>2</sub>L, SnH(OH)L<sup>2-</sup> where L represents tetravalent citrate ligand. However, the most commonly observed complex in

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