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Effect of various additives on morphological and structural characteristics of pulse electrodeposited tin coatings from stannous sulfate electrolyte

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ABSTRACT

The pulse electrodeposited tin coatings are synthesized from an acidic electrolyte (stannous sulfate, $SnSO_4$30 g/L and sulfuric acid, H_2SO_4—200 g/L) containing various additives (polyethylene glycol (PEG), thiourea and Triton X-100). The effect of the additives on surface morphology, preferred orientation of grains, grain size, and surface roughness has been studied. The final coatings are characterized by X-ray diffractometry (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), and surface profilometry. In the absence of additives, tin deposition is associated with prominent hydrogen evolution reaction giving rise to rough deposits. Both PEG and thiourea act as grain refiner while Triton X-100 acts as a brightener in the electrolyte. The cathodic polarization on the reduction of the tin (II) ions is more pronounced when a combination of additives is used and further, fine-grained, smooth and shiny electrodeposits of tin are obtained due to a synergistic effect of the adsorbed species.

1. Introduction

Pulse electroplating of pure tin is one of the hottest topic of current research worldwide. Pure tin possesses excellent solderability, high corrosion and oxidation resistance, and has potential applications in microelectronic industry. Conventional lead tin plating is being avoided now a days due to its harmful effect on human life and environment [1–3] . In general, two most popular types of electrolytes used in tin electroplating are (1) alkaline stannate based electrolyte and (2) acidic stannous sulfate based electrolytes [4,5]. Other electrolytes, i.e., citrate electrolyte, pyrophosphate electrolyte and methyl sulfonic acid (MSA) electrolytes have also been reported in the literature [6–8].

Porous, rough, dendritic, and needle-like tin electrodeposits are obtained from acidic stannous sulfate electrolytes when additives are absent in the electrolyte. For better surface finish, morphology and full cathode coverage during acidic tin electroplating, various organic chemicals known as additives have been added to the electrolyte. It has been noticed that these organic chemicals such as surface active agent, linear and/or aromatic compounds, and sulfonic acid products are necessary components of electrolyte [9–12]. There may be a single component additive or may contain several components like sorbitol, polyethylene glycol, gelatin, gluconate, etc. [7,13–15]. These additives should be added to the electrolyte in optimum level as an excess quantity may cause uncontrolled deposition kinetics. The surface active agents are also added to relieve the deposit stress. For instance, Triton X-100 improves the surface morphology and provides better plating finish, and has been used as an additive in few reports [9,10]. Thiourea and PEG have been added in the past but not investigated in detail for tin coatings. The purpose of this entire investigation is to electrodeposit tin coatings on copper substrates from acidic electrolytes and to study the changes in the surface morphology and microstructural properties with respect to different additives (PEG, thiourea, Triton X-100 and a combination of these).

2. Experimental methods

The chemicals used in the present study are of reagent grade (Loba chemie, 99.9%) stannous sulfate, $SnSO_4$ and sulfuric acid, H_2SO_4. The compositions are shown in Table 1. The plating bath is prepared by dissolving $SnSO_4$ in deionized water first, followed by the addition of H_2SO_4 gradually, as the reaction is highly exothermic. The solution is stirred until the stannous salt is almost dissolved. Three types of organic additives (1) Triton X-100 ($C_8H_{17}C_6H_4(OCH_2CH_2)_nOH$, $n = 9$–10 with average molar mass

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Table 1
Bath compositions.

Bath	Composition (g/L)	Additive (g/L)	
A	Stannous sulfate (30)	Sulfuric acid (200)	Nil
B	Stannous sulfate (30)	Sulfuric acid (200)	PEG (1.0)
C	Stannous sulfate (30)	Sulfuric acid (200)	Thiourea (0.5)
D	Stannous sulfate (30)	Sulfuric acid (200)	Triton X-100 (0.1)
B + C	Stannous sulfate (30)	Sulfuric acid (200)	PEG (1.0) + thiourea (0.5)
B + C + D	Stannous sulfate (30)	Sulfuric acid (200)	PEG (1.0) + thiourea (0.5) + Triton X-100 (0.1)

625 g/mol, (2) polyethylene glycol, $H(CH_2CH_2O)_nOH$, $n = 8000$ with average molar mass of 8000 g/mol, and (3) thiourea, CH_4N_2S, with a molar mass ~76 g/mol. All chemicals are of reagent grade (Sigma Aldrich, 99.8%).

A 0.5-mm thick copper foil (Merck Specialties Pvt. Ltd., electrolytic grade, 99.8%) with 6 cm^2 surface area is used as the cathode. The copper foil is washed with 10% dil. H_2SO_4 to remove the inherent oxide layer, and then ultrasonicated for 30 min to remove any foreign impurity. Tin metal plate (Merck Specialties Pvt. Ltd., electrolytic grade, 99.8%) with approximately 10 cm^2 surface area is used as the anode.

Electrochemical measurements have been carried out using an Autolab PGSTAT 30 potentiostat–galvanostat with a 10 A current booster. The pH of the solution is 2.3. Current/potential curves under galvanostatic conditions are obtained directly on the computer by Eco Chemie software module. The cathodic scan rate is 1 mV/s. A typical generated pulse waveform is shown in Fig. 1, where the duty cycle is 9% with on time of 0.001 s and off time of 0.01 s. The plating duration is 24 min and thickness of the coatings is around 12 μm.

Surface roughness is measured using a Veeco DEKTAK 150 surface profilometer with a diamond shaped stylus which measures the vertical displacement produced during its scan over the surface projections.

Cathodic current efficiency (CCE) is calculated using the following equation:

$$\mathrm{CCE}\ \ (\%) = 100 \quad \times \quad \frac{M_a}{M_t} \tag{1}$$

where M_a is the actual amount of metal deposited and M_t is the amount calculated theoretically from Faraday's laws [4].

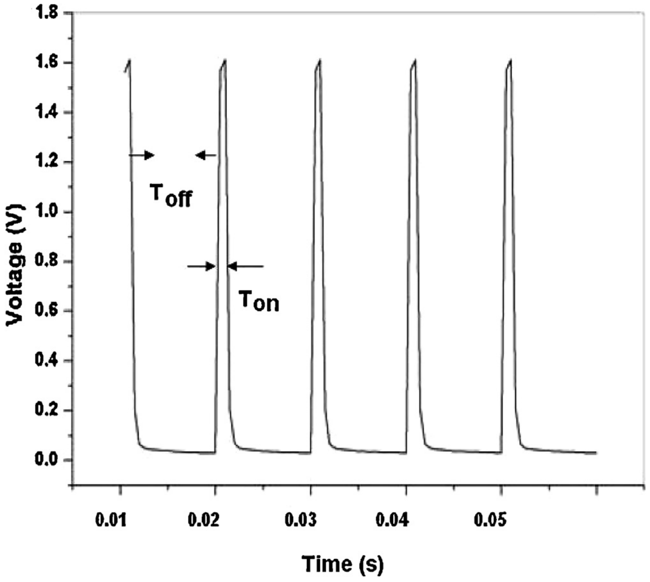

Fig. 1. DC square waveform used for cathodic pulse electrodeposition.

Pulse electrodeposited films are analyzed using scanning electron microscopy (SEM, Carl Zeiss Supra) equipped with an ultra thin window (UTW) energy dispersive X-ray (EDX) detector. The crystal structure is characterized using X-ray diffraction machine (Brucker's X-ray diffractometer, D8 Advance) with a vertical goniometer and a Co target operating at 40 kV and 35 mA with a K_α wavelength of 0.178 nm. The crystallite size of the deposits is estimated by the Scherer formula and the texture coefficients of various planes are calculated by using the following Eq. (2) [6]:

$$T_c = \frac{(I_{hkl})/(I_{hkl}^{std})}{1/n\sum_{hkl}(I_{hkl})/(I_{hkl}^{std})} \tag{2}$$

where I_{hkl} is the measured intensity of reflection *hkl* and I_{hkl}^{std} is the *hkl* reflection intensity of the standard sample, and n is the number of reflections. If the texture coefficient (T_c) is greater than 1.0, it indicates the existence of a preferred orientation.

The 3D surface images are observed using Atomic Force Microscopy (Dimension 3100 Digital Instruments AFM).

3. Results

3.1. Polarization measurements

It is clear from the typical voltammogram, as shown in Fig. 2, that the formation of isolated nuclei takes place at around −500 mV.

As the current density increases further all the curves show a typical peak followed by a steady state region before the hydrogen evolution is established. In bath A, the reduction of tin ions occurs at ~ -460 mV. The current density rises rapidly fast with potential and hydrogen evolution begins. Thus, the steady state region is very narrow signifying poor cathode coverage and lower current efficiency. When PEG is added (curve B) a striking feature is noticed. There is a negative shift in the reduction potential of tin. This negative shift in the reduction potential to −480 mV for tin (in the presence of

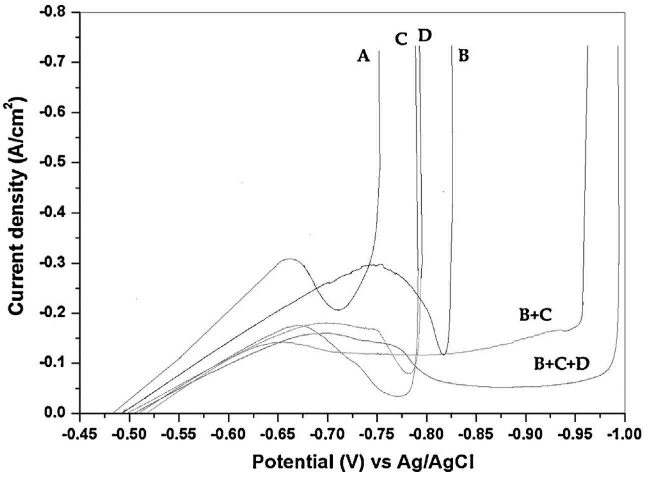

Fig. 2. Cathodic polarization curves of tin from various baths (a) bath A, (b) bath B, (c) bath C, (d) bath D, (e) bath B + C, and (f) bath B + C + D.