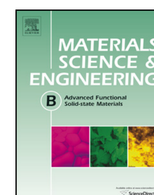
Materials Science and Engineering B 190 (2014) 104–110

Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb



Characterization of tin films synthesized from ethaline deep eutectic solvent

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ARTICLE INFO

Article history:
Received 8 April 2014
Received in revised form 5 September 2014
Accepted 18 September 2014
Available online 1 October 2014

Keywords:
Tin
Electrodeposition
Choline chloride
Ethaline
Deep eutectic solvent

ABSTRACT

Tin (Sn) films were electrodeposited by galvanostatic method from ethaline deep eutectic solvent (DES), without any additives. The effect of various deposition parameters on the microstructure was studied. With increase in metal salt concentration from 0.01 to 0.1 M, changes in current–potential behaviour were observed in the polarization scans. This might be due to the existence of $[SnCl_3]^-$, $[Sn_2Cl_5]^-$ complexes in ethaline DES. Smooth and homogeneous deposits were obtained on a steel substrate surface by applying current density of 1.57×10^{-3} A/cm^2 at 25 °C. Under these conditions the deposition rate was found to be $0.1 \pm 10\%$ μm/min and current efficiency was obtained as $84 \pm 3\%$. XRD analysis of the deposit confirmed the polycrystalline tetragonal structure with mostly (2 0 0) orientation having a crystallite size about $62 \pm 16\%$ nm along with an internal strain of $0.0031 \pm 22\%$. The present deposition method is simple, economical and can be adapted for industrial applications.

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1. Introduction

Tin (Sn) films have been electrodeposited from a range of aqueous acidic and alkaline baths for a variety of applications [1,2]. These baths are widely used for their low cost, high throwing power [2,3], high current efficiency [2–5] and their ability to operate at higher current density [2]. However, these baths require various additives and reagents [6,7]; as a result different toxic end products [2] may be formed due to their use. These toxic end products may have environmental impact and they need to be neutralized. Moreover, the highly corrosive nature of these baths restricts their applications due to health and safety issues [2,8,9]. In addition to this, oxidation of Sn(II) to Sn(IV) initiates the formation of SnO_2 and $Sn(OH)_6$. These compounds ultimately lead to sludge formation and reduction in deposit yield along with the decrease in current efficiency [2,8,10].

Ionic liquid (IL) could be a viable option over aqueous electrolytes to overcome the above existing issues and problems on Sn electrodeposition. An IL is defined as ‘a liquid consisting solely of cations and anions with a melting point of 100 °C and below’ [11]. Considerable research has been undertaken during the past decade for the development of ILs, details of which are available in numerous books and reviews [11–13]. Some of these ionic liquids has also been employed for metal deposition [12,14].

Among all types of ILs, choline chloride (ChCl) based ILs has been identified as the most efficient electrolyte for practical plating purposes. Low cost [12], low toxicity, low viscosity [15], higher solubility of metals [16,17] and ease of preparation [17] are the attractive properties of ChCl based ILs. ChCl based ILs consist of $C_5H_{14}NOCl$ (choline chloride) with a hydrogen bond donor (HBD) such as CH_4N_2O (urea), $C_2H_2O_4$ (oxalic acid), $C_3H_8O_3$ (glycerol), $CH_2(COOH)_2$ (malonic acid), $C_2H_6O_2$ (ethylene glycol) [12,18,19] to form a deep eutectic solvent (DES) [12]. Currently a DES based on choline chloride and ethylene glycol, available commercially and also known as ethaline has been chosen for tin electrodeposition.

For practical plating purposes it is essential to acquire an understanding of the electrochemistry of Sn in ILs specifically in ChCl based ILs. Previous electrochemical studies on Sn have been reported using a variety of ILs [20–28]. Voltammetry studies have highlighted the reduction of Sn(II) to Sn(0) by a single step for two electron transfers irrespective of bath temperature or substrates [20–22,26–28].The reduction of Sn is electrochemically quasi-reversible in aluminium chloride-1-methyl-3-ethylimidazolium chloride ($[AlCl_3$-MeEtimCl$]$) [21], irreversible in 1-ethyl-3-methylimidazolium tetrafluoroborate [EMI-BF_4] [26] and reversible in ChCl–urea system [29].

The reduction reaction of Sn in ethaline DES corresponds to an irreversible system, as has been reported in our previous paper [30]. The presence of various Sn species in these systems might be responsible for various voltammetric responses. Various Sn

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http://dx.doi.org/10.1016/j.mseb.2014.09.014
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complexes like $[SnCl_2(DCA)_y]^{(y-2)-}$, $[Sn\ (DCA)_xCl_z]^{(x+z-2)-}$, $[SnCl_3]^-$, $[SnCl_4]^{2-}$ were reported for electrochemical studies in 1-ethyl-3-methylimidazolium dicyanide ([EMI-DCA]), [$AlCl_3$-MeEtimCl], zinc chloride-1-ethyl-3-methyl-imidazolium chloride ([$ZnCl_2$-EMIC]) and [EMI-BF_4] [20–22,26]. Complexes like $SnCl_3^-$ and $Sn_2Cl_5^-$ have been reported in ChCl DES mixture [29–32]. In addition, the concentration of $SnCl_2$ and HBD of the DES mixture plays an important role in complex formation [29]. For practical plating purposes metal deposition is carried out using maximum plating current which is only possible by incorporating the electrolyte with maximum metal ions. However, studies on the electrochemical aspects of Sn with concentration higher than 0.05 M at room temperature are not available in the current literature. Room temperature deposition is an efficient method to produce deposits without high energy consumption. This unsolved issue is addressed in the present research paper.

Previously Sn deposits obtained from various ILs were porous or sometimes even a discontinuous film [20,22,26]. Deposit morphology was improved by adding various additives in the electrolyte [33]. Bath temperature is another important factor in the variation of deposit quality [20–22]. Dense, smooth and adherent deposits were obtained from 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMP-TFSI) [23] at 25 °C whilst porous deposits were obtained from other ILs [22] at elevated temperatures. Researchers also reported about the deposition of some dendritic clusters of Sn from reline (ChCl-urea) at an applied plating current of 0.01 A/cm^2 [29]. Smooth, bright and adherent Sn deposits were reported when deposition was carried out on Cu and mild steel substrates from various DES at 40 °C and 90 °C [34], but contained SnO_2 and were plated at low current efficiency [34]. Therefore in the current literature the maximum plating current or related parameters for deposition at room temperature from DES are not available.

In order to fill the gap in information on electrochemical behaviour of Sn in ethaline DES, polarization scans were carried in Pt rotating disc electrode (RDE). For these analyses hydrated $SnCl_2$ was added in a concentration range of 0.01–0.1 M, since hydrated salts are easily available and used in industrial metal plating. In these experiments neither any additives nor any reagents were used during electrodeposition. The operating temperature was maintained in a range of 25–55 °C with various agitation rates to monitor the effect of temperature and agitation on mass transfer rate. Thereafter, Sn deposition was carried out using stainless steel substrates by galvanostatic method. Various deposition parameters such as growth rate, current efficiency, grain structure and its crystalline structure were studied.

2. Experimental

The ethaline melt was prepared by mixing of choline chloride and ethylene glycol (supplied by Sigma Aldrich) in 1:2 ratio and then the mixture was kept in a thermostatic heater at 40 °C and stirred for 24 h to form a colourless liquid. After this preparation, the electrolyte was stored in an airtight glass bottle to minimize the interaction of the electrolyte with atmosphere. Later on, between 0.01 and 0.1 M $SnCl_2{\cdot}2H_2O$ was added into this melt at 25 °C. A thin powdery layer formation was observed over the electrolyte surface, when the metal salt concentration exceeded 0.1 M, showing this to be the solubility limit for $SnCl_2.H_2O$ in this melt. Reagent grade (purity 98%) chemicals were used for all experiments.

To determine the reduction potential and maximum current for tin deposition polarization scans were carried out. For these polarization scans μAutolab Type II potentiostat/galvanostat instrument along with software named General Purpose Electrochemical System (GPES) were used. The scans were carried out in a water jacketed three electrode cell, where the platinum rotating disc electrode (RDE) served as a working electrode, platinum mesh as a counter electrode and silver wire as a reference electrode [35]. These scans were carried out in a scan range of −0.7 V to 0.6 V where the RDE speed was maintained in the range of 300–2000 rpm at a temperature range of 25–55 °C. Thereafter to determine the stripping currents of the polarization scans, anodic stripping voltammetry (ASV) was carried out using 0.1 M $SnCl_2{\bullet}2H_2O$. In these experiments, the deposition was carried out in a scan range of −0.45 to −0.6 V for 180 s followed by stripping voltammetry in a scan range of −0.4 to 0 V. These experiments were performed by maintaining RDE speed of 300 rpm at 25 °C.

Finally a set of deposition experiments were carried out to ascertain the deposit properties. A 0.9 cm diameter low carbon steel disc was used in a rotating disc (RD) apparatus as the substrate material. This disc is detachable from RD apparatus which helps in polishing and inspection of the substrate before and after the operation. Electrodeposition was performed using a PL320 constant power supply (Thurlby-Thandar) and a TM356 digital multimeter (Thandar). The cell arrangement for deposition experiments was reported in our earlier paper [35]. Deposition was performed in RDE speed ranging from700 to 1300 rpm at a temperature range of 25–45 °C. The deposition duration was selected between 1800 and 7200 s in order to achieve a deposition layer between 3 and 12 μm thick. The deposit morphology was examined using an Olympus BX41 optical microscope, Hitachi S2400 Scanning Electron Microscope. Crystal structure was determined using Philips PW3040/60 X-ray diffractometer. For reproducibility and error measurements, each experiment was carried out at least three times.

3. Results and discussion

3.1. Electrochemical polarization

Fig. 1 shows the polarization scan for Sn reduction at Pt electrode from various concentrations of $SnCl_2{\cdot}2H_2O$ in ethaline DES. The reduction process starts at a potential of −0.36 V and reaches a limiting current beyond a potential of −0.4 V. The limiting current for Sn^0 deposition was determined from the flat plateau region of the forward scan. In the reverse sweep the oxidation process commences at −0.36 V followed by a stripping peak at −0.25 V for 0.01 M $SnCl_2{\cdot}2H_2O$. This stripping peak shifts in the positive direction with increase in metal salt concentration. This single reduction

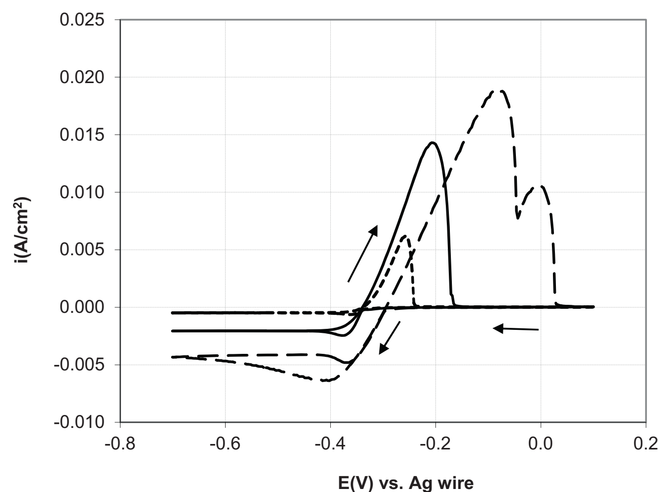

Fig. 1. Polarization scans on ethaline DES containing various concentration of $SnCl_2{\cdot}2H_2O$ at 35 °C and 300 rpm, scan rate 0.01 V/s, (···) 0.01 M $SnCl_2{\cdot}2H_2O$, (—) 0.05 M $SnCl_2{\cdot}2H_2O$, (– –) 0.1 M $SnCl_2{\cdot}2H_2O$.

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