Article

Electrodeposition of Sn–In Alloys Involving Deep Eutectic Solvents

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Received: 1 November 2019; Accepted: 27 November 2019; Published: 28 November 2019

Abstract: Tin–indium alloys represent attractive lead-free solder candidates. They show lower values of melting point than pure indium, so that they are investigated as materials with significant applications potential in the electronic industry. Electrodeposition is a very convenient route to prepare Sn–In alloys. The paper presents several experimental results regarding the electrodeposition of Sn–In alloy coatings involving deep eutectic solvents (DESs), namely using choline chloride–ethylene glycol eutectic mixtures. The influence of the main operating parameters on the Sn–In alloy composition and characteristics are presented. Adherent and uniform Sn–In alloy deposits containing 10–65 wt % In have been obtained on Cu substrates. The In content was found to increase as both the In:Sn molar concentration ratio of ionic species in the electrolyte and the applied temperature increased. The use of pulsed current allowed the use of higher current densities leading to slightly higher values of In content in the alloy deposit. X-ray diffraction (XRD) analysis revealed the presence of InSn₄ and In₃Sn phases in agreement with the phase diagram. According to thermogravimetric analysis (TGA) measurements, values of melting points in the range of 118.6 and 127.5 °C were obtained depending on the alloy composition. The solder joints' behavior and alloy coatings corrosion performance were also discussed.

Keywords: electrodeposition; Sn–In alloy; deep eutectic solvents; lead-free solder alloy; pulse plating

1. Introduction

Several years back and motivated by environmental and health concerns, the legislation regarding the end-of-life disposal and the European Union's (EU) Restriction of Hazardous Substances (RoHS) Directive determined the elimination of SnPb solder from all electronic applications in the EU and other countries' markets, including China, Japan, South Korea, Turkey and the United States [1,2]. Under these circumstances, the development of lead-free solder alloys attracted increased interest. Currently, a large range of solders as binary and ternary alloys have been proposed, based on Sn coupled with other elements such as Cu, Ag, Zn, Ni, Sb, Bi and In [2–7].

The most common solder alloys, such as Sn–Ag and Sn–Cu solder alloys have melting point temperatures higher than 200 °C (221 and 227 °C, respectively) while for low-temperature soldering conditions, only Sn–Bi and Sn–In systems may be used, whose melting points are below 180 °C (138–170 and 118–145 °C, respectively) [2,8,9].

On the other hand, a major problem affecting reliability aspects particularly in long-life electronic applications is represented by the tin whiskers. Usually, they represent crystalline filaments 1–10 μm thick and up to hundreds of microns long, which can grow from any high-Sn solder or coating, causing short circuits. Specific environmental conditions, such as power cycling, thermal, humidity conditions could cause tin whisker formation, although this is still being debated in the literature [2]. Various substitute approaches that mitigate the whiskers growth of Sn include the use of Bi, of Ni underlayer or of conformal coatings [9–12].

Quite recently it has been shown that the addition of a certain amount of In can contribute to the elimination of whiskers growth in electrodeposited Sn on copper substrates under ambient temperature aging. Therefore, in terms of Sn whisker mitigation, In seems to represent a better additive than Pb [9,13,14]. In addition, due to their physico-mechanical and chemical properties, including low melting temperature, low stress, superior thermal fatigue resistance, Sn–In alloys are suitable for making connections by soldering in the assembly of integrated circuits and micromodules [15–17]. Besides their use as lead-free solder alternative, the Sn–In alloys are also attractive as protective, antifriction and wear-resistant coatings and, more recently, as an efficient catalyst for the electrochemical reduction of CO_2 [15,18–20].

Electrodeposition is a very convenient route to apply Sn and Sn alloys, due to its advantages such as compatibility with photolithography, high deposition rate, ease in extending substrate size, being environmentally benign and its good end properties [5]. However, the traditional use of aqueous electrolytes scarcely delivers the desired composition and due to the stannous oxidation problems the baths show poor stability. In the case of Sn–In alloy electrodeposition in particular, additional difficulties have been noticed mostly associated with the quite large difference between the standard electrode potentials of the Sn/Sn^{2+} and In/In^{3+} half-cells [9].

The electrodeposition of Sn–In alloys in aqueous solutions usually involves either strongly acidic or alkaline electrolytes, both containing alkali metal salts of carboxylic acids as chelating agents to ease the Sn deposition. A better stability and control of the plating process has been noticed in the case of alkaline baths [21]. Acidic sulfate based electrolytes have been also applied to electrodeposit Sn–In alloys, usually in the presence of several organic additives to facilitate obtaining bright coatings. [15,22]. Ozga et al. [23] studied the electrodeposition of Sn–In alloy involving a complex citrate type electrolyte with additions of PEG 3000 nonionic surfactant at $\text{pH} = 2.5$. Quite recently, Mahapatra and Dutta [9] reported the electrodeposition of Sn–In alloy involving a methanesulfonic acid based electrolyte which allowed coatings containing up to 20% In to be obtained. In addition, it has been concluded that alloying Sn with a certain percentage of In followed by a heat treatment eliminates the whiskers growth from Sn coatings under room temperature aging conditions.

In spite of the adequate performance, the preparation involving aqueous solutions usually suffers from some drawbacks, mainly related to the complexity and sometimes toxicity of the electrolytes formulation, the need for additives, as well as the occurrence of hydrogen evolution as secondary reaction affecting the cathodic efficiency. Moreover, to keep the chemical composition of the alloy constant during the electrodeposition process is quite challenging, mostly due to the variance in the redox potentials of the constituent metals or/and variation of deposition kinetics of one metal relative to the other one [24,25].

To overcome these critical aspects, deep eutectic solvents (DESs), which are a new class of ionic liquids, have been used for the electrodeposition of a large range of metals and alloys. They possess several favorable characteristics such as low vapor pressure, wide liquid-phase range and greater electrochemical and thermal stability, low cost, and being stable against moisture, and are also considered as more environmentally friendly alternatives [25–27]. DESs are composed of binary mixtures of quaternary ammonium salts with either a hydrogen bond donor such as urea, ethylene glycol, glycerol, malonic acid, oxalic acid or a metal salt [26,28–30].

Only a few investigations related to the electrodeposition of binary and ternary Sn and/or In alloys from DESs have been reported. Gao et al. [31] studied the electrodeposition of Sn–Bi alloy

from a choline chloride-ethylene glycol deep eutectic solvent. The results suggested the possibility of electroplating the Sn–Bi alloys with their composition around the eutectic point. The influence of the choline chloride eutectics composition on the properties of Sn and Sn–Ni alloys has been also evidenced in [32]. In the case of Zn–Sn alloys, their morphology and composition can be changed by judicious choice of the DES containing electrolyte composition [33]. Shaban et al. [24] successfully electrodeposited Sn–Ag alloys involving choline chloride-ethylene glycol eutectic mixtures. The concentration of silver ions in the DES electrolyte was the main factor affecting the crystallites size and morphology of the Sn–Ag alloys.

Recently, the electrodeposition of In on Cu [34] and W [34,35] substrates was reported by using the deep eutectic solvent choline chloride-ethylene glycol (1:2).

The electrodeposition of Cu–In alloys from choline chloride-urea eutectic mixture onto Mo substrates has been reported in [36]. It was concluded that the composition of the deposited films depends on both deposition potential and on the concentration ratio of the metal cations in the ionic liquid. The same group also studied the one step electrodeposition of Cu, In and Ga metals and their alloys from the choline chloride:urea eutectic mixture [37]. The morphology of the deposits depended primarily on the metal salt concentration in solution, since dendrites as well as compact layers were obtained. Moreover, the formation of the ternary alloys was found to be very limited and thus the alloying mechanism was dominated by the Cu–Ga and Cu–In binaries.

Very few published works discussed the electrodeposition of Sn–In alloys involving traditional ionic liquids. The group of Morimitsu and Matsunaga [38,39] investigated the electrochemical processes of Sn, In and In–Sn in EMI-BF₄-Cl melts obtained by mixing of EMIC(1-ethyl-3-methylimidazolium chloride) and NaBF₄ in 60:40 mol % ratio. The results obtained suggested that the deposition proceeds via an underpotential deposition of In on the Sn predeposited electrode surface. Two crystalline phases (Sn and InSn₄) have been evidenced, in which the crystallinity of InSn₄ was more improved by increasing the deposition temperature to 80 °C. The same group has also reported the influence of current pulses on the In–Sn electrodeposition from EMI-BF₄-Cl system [40]. In–Sn deposits with higher indium content were obtained by the pulsed technique. For electrolytes containing higher concentrations of the stannous ion, the indium content decreased with the off-time duration, probably due to the exchange reaction between indium metal in deposits and stannous ion in melt during off-time. Therefore, the required composition of the In–Sn alloy coatings may be obtained through a proper selection of the pulse parameters.

Considering the above, the present paper aims to explore the feasibility of the co-electrodeposition of Sn–In alloy coatings involving DESs, mainly using choline chloride-ethylene glycol eutectic mixtures. It is worth mentioning here that to the best of our knowledge this is the first investigation reporting the electrochemical deposition of Sn–In alloys using DES based electrolytes. The influence of the main operating parameters (i.e., the metallic ions concentration ratio, the current form: direct or pulse current, temperature) on the Sn–In alloy composition and characteristics are presented. The solderability performance as well as corrosion behavior in 0.5 M NaCl aqueous solution exposure are reported as well.

2. Materials and Methods

To perform experiments, choline chloride-ethylene glycol eutectic mixtures (1:2 molar ratio) (denoted ILEG), containing the metallic salts corresponding to the metal/alloy that is to be electrodeposited, were synthesized as shown in Table 1. Choline chloride (HOC₂H₄N(CH₃)₃Cl) (ChCl) (Aldrich, 99%), ethylene glycol (EG) (Aldrich, 99.5%), tin chloride (SnCl₂·2H₂O) (Aldrich, 98%) and indium chloride (InCl₃) (Aldrich, 98%) were used as received.

The eutectic mixture (called ILEG) was prepared by mixing and heating reagents in the stated proportions at 80–100 °C, with gentle stirring until a homogeneous, clear liquid was formed.

Table 1. Electrolytes composition and operating parameters.

Electrolyte Type	Electrolyte Composition	Temperature/°C
ILEG-SnIn	0.05 M InCl ₃ + 0.05 M SnCl ₂ ·2H ₂ O	20–60
	0.1 M InCl ₃ + 0.05 M SnCl ₂ ·2H ₂ O	
	0.1 M InCl ₃ + 0.03 M SnCl ₂ ·2H ₂ O	
	in ILEG	

Bulk electrodeposition of the Sn–In alloys has been performed under mild stirring and galvanostatic (current control) conditions using a DC/pulse reverse power supply (pe86CB 3HE, Plating Electronic GmbH, Sexau, Germany) and a two-electrode cell configuration. The copper metallic substrates used (70 mm × 35 mm × 0.2 mm) were initially subjected to a mechanical polishing using 1000 and 2000 abrasive paper, followed by chemical pickling in 1:1 HNO₃: H₂O solution at 25 °C for 20–30 s, then rinsed with running water and distilled water and air dried. Platinized titanium plates were used as anodes. Current densities between 1 and 25 mA cm^{−2} and electrolyte temperatures between 25–65 °C were applied for electrodeposition durations between 20 and 60 min.

The morphology and elemental composition of the deposited Sn–In alloys were examined using scanning electron microscopy (SEM) associated with energy-dispersive X-ray spectroscopy (EDX) (SU8230, HITACHI High-Technologies Corp., Tokyo, Japan equipped with EDX Oxford detector analyzer). The phase composition and structure were determined involving X-ray diffractometry (XRD) (High Resolution SmartLab X-ray diffractometer Rigaku, Tokyo, Japan 9 kW, with rotating anode) using CuK α radiation, at a speed of 2 s/step (1 step = 0.05°).

Thermogravimetric analysis (TGA) (STA 8000, Perkin Elmer, Waltham, Massachusetts, USA) was applied in order to determine the melting point of the electrodeposited alloys.

The solderability performance was assessed by dipping in molten SAC 305 (Sn3.0Ag0.5Cu) alloy and by measurement of the angle of wettability that provides information on the degree of solder contact and strength of the solder joint, according to IPC-TM-650 [41] and IPC-610E [42] procedures.

The corrosion behavior of the electrodeposited Sn–In alloy coatings was assessed involving accelerated laboratory tests in aerated 0.5 M NaCl aqueous solution, respectively: (i) continuous immersion at 25 °C for 360 h with intermediary visual examinations, (ii) potentiodynamic polarization curves at 3 mV s^{−1} sweep rate, and (iii) electrochemical impedance spectra (EIS) at open-circuit potential. A minimum of 3 pieces of the deposited Sn–In alloy on a copper metallic support (70 mm × 35 mm) were subjected to immersion tests. The coating thickness was 10 ± 2 μ m and it was determined according to IPC-TM-650 procedure, Method 2.2.5 [43]. The geometrical surface of working electrode in the electrochemical tests was 0.63 cm², the counterelectrode was a Pt mesh and a Ag/AgCl/KCl sat. has been used as reference electrode. EIS spectra, recorded with 10 mV ac voltage within 100–50 mHz frequency range, were processed using ZView 2.4 software from Scribner Association Inc., Derek Johnson.

3. Results and Discussion

To synthesize the electrodeposition electrolytes having the metal concentrations according to Table 1, the corresponding amounts of SnCl₂·2H₂O and InCl₃ were added to ILEG solvent under mild stirring. All mixtures are liquid at room temperature (25 °C). The liquids were colorless and clear, with electrical conductivities in the range of 2–12 mS cm^{−1} for a temperature domain between 25 and 75 °C. Viscosity values between 35 and 7 mPa·s have been determined for the same range of temperature, quite comparable with those of the pure ILEG solvent. The determined values of activation energies for viscosity (E_η) from Arrhenius plots of viscosity vs. 1/T were around 25 kJ·mol^{−1}, relatively larger than those characteristic to high temperature molten salts.

3.1. Sn–In Alloy Coatings Characteristics

The Sn–In alloy electrodeposition onto a Cu substrate using ILEG–SnIn electrolyte was performed under galvanostatic conditions, for applied current densities in the range of $2\text{--}25\text{ mA}\cdot\text{cm}^{-2}$, at temperatures between 25 and $65\text{ }^{\circ}\text{C}$, under mild stirring. Smooth, adherent gray deposits were obtained, with a semi-bright appearance. Deposition rates between 0.08 and $0.15\text{ }\mu\text{m}\cdot\text{min}^{-1}$ were determined for the investigated current density domain.

Figure 1 shows examples of the Sn–In alloy morphologies for different electrolyte compositions and current density values, at a temperature of $60\text{ }^{\circ}\text{C}$.

Figure 1. Scanning electron microscope (SEM) micrographs of Sn–In alloy electrodeposited from ILEG–SnIn system at $60\text{ }^{\circ}\text{C}$ containing: (a) $50\text{ mM InCl}_3 + 50\text{ mM SnCl}_2$, $2.5\text{ mA}\cdot\text{cm}^{-2}$; (b) $100\text{ mM InCl}_3 + 30\text{ mM SnCl}_2$, $2.5\text{ mA}\cdot\text{cm}^{-2}$; (c) $100\text{ mM InCl}_3 + 30\text{ mM SnCl}_2$, $10\text{ mA}\cdot\text{cm}^{-2}$ (Cu metallic substrate).

As shown in this Figure, the surface morphology depends on both the concentration of the metallic species in the electrolyte and on the applied current density. Generally, the Sn–In alloy deposit was quite homogeneous, consisting of irregular tetragonal-like particles of about $1\text{--}2.5\text{ }\mu\text{m}$, entirely covering the metallic substrate. As the In:Sn molar ratio of salts in the electrolyte increased (higher In content) at a constant applied current density the constituent particles became smaller, i.e., from the order of $2\text{--}2.5\text{ }\mu\text{m}$ for the In:Sn ratio of 1, towards $1.5\text{--}2\text{ }\mu\text{m}$ up to about $1\text{--}1.5\text{ }\mu\text{m}$ for In:Sn ratios of 2 and 3, respectively.

This change might be related to the increase of In content in the alloy as Figure 2a below showed, which may determine the loss of their well-defined edges. In addition, the use of a higher current density determined the formation of more uniform elongated particles.

Figure 2. Cont.

Figure 2. The influence of: (a) In:Sn molar ratio of dissolved salts in electrolyte; (b) current density; (c) temperature, on indium content within the alloy electrodeposit.

The chemical analysis of the Sn–In alloy coatings obtained was performed by EDX. The influence of the main operation parameters, respectively of the In:Sn molar ratio in the electrolyte, the current density and temperature on the indium content in the deposit is illustrated in Figure 2.

As shown in Figure 2a, the increase of In:Sn molar ratio in the electrolyte from 1.0 to 3.0 facilitated a higher In content in the deposit, from 30–35% to 60–63% (wt %).

This behavior may be related to the influence of mass transport occurring in electrolytes with higher concentrations of InCl_3 . The preliminary voltammetry studies recorded on Cu electrode (not shown here) revealed that the deposition potential of In metal is more negative than that of Sn metal, suggesting that an In(III) concentration higher than that of Sn(II) in the bath may determine an increased In content in the alloy.

A decrease of the In content vs. the applied current density was also observed for two constant values of the In:Sn molar ratios in the bath, respectively from 55–60% In at $2.5 \text{ mA}\cdot\text{cm}^{-2}$ to around 12–20% In at $10 \text{ mA}\cdot\text{cm}^{-2}$, at 60°C (Figure 2b). According to Alcanfor et al. [35], the diffusion coefficient of In^{3+} in choline chloride-ethylene glycol is in the range $3.7\text{--}5.8 \times 10^{-12} \text{ m}^2\cdot\text{s}^{-1}$, one order of magnitude lower as compared to the diffusion coefficient of Sn^{2+} , of about $1.96 \times 10^{-11} \text{ m}^2\cdot\text{s}^{-1}$ as reported by Ghosh et al. [44] in the same DES. Therefore, as the applied current density increased, the amount of tin species transported to the cathode surface will be higher, thus determining an enrichment of Sn content in the alloy.

Higher values of the applied temperature, facilitate an increased content of In in the alloy, which was more pronounced in the temperature range of $25\text{--}40^\circ\text{C}$, as illustrated in Figure 2c. This behavior is determined by the decrease of the viscosity of the electrolyte with the temperature, which consequently facilitates a faster diffusion of the In(III) species towards the electrode surface, thus producing an increased In content in the alloy [35]. This behavior is also in agreement with findings in references [15,22] during Sn–In alloy electrodeposition from aqueous sulfate electrolytes.

In order to improve the quality of the electrodeposited Sn–In alloy coatings from morphological and homogeneity viewpoints, the use of pulsed current (PC) was also explored.

It is known that the PC may have a beneficial influence on morphology, microstructure, ductility, hardness of the electrodeposited layers while allowing higher values of the applied current density. The use of PC during electrodeposition processes in DESs based electrolytes has been scarcely reported. Maharaja et al. [45] reported the use of PC for Cr and Cr/single-walled carbon nanotubes (SWCNT) composite coatings deposition from a DES consisting of choline chloride, $\text{CrCl}_3\cdot 6\text{H}_2\text{O}$, ethylene glycol and KCl with additions of $2 \text{ g}\cdot\text{L}^{-1}$ SWCNT. A more uniform Cr nanostructured deposit, with a much more uniform incorporation of SWCNT in the coating has been evidenced on applying PC. Manolova et al. [46,47] applied PC during Pd and Pd–Ag alloy electrodeposition from choline chloride:urea eutectic mixtures, also in the presence of different additives. SEM investigations have shown that the use of PC facilitated an increased metal deposition rate and improved the quality of the deposited Pd and Pd–Ag layers.

Under these circumstances, several experiments were performed in order to explore the influence of PC on the characteristics of the electrodeposited Sn–In alloy coatings. The square-wave current pulses used in the PC experiments had average current densities between 5 and 25 mA·cm^{−2} and on-/off-times of $t_{on}/t_{off} = 50$ ms/50 ms.

Figure 3 presents an example of the obtained morphology of Sn–In alloy deposit under the aforementioned PC conditions and the spatial distribution profiles for the main elemental components.

Figure 3. SEM micrographs of Sn–In alloy electrodeposited from ILEG-SnIn system at 60 °C containing: 100 mM InCl₃ + 50 mM SnCl₂, 10 mA·cm^{−2} $t_{on} = t_{off} = 50$ ms (Cu metallic substrate: (a), (b) SEM images at different magnifications; (c) energy-dispersive X-ray spectroscopy (EDX) maps of elemental distribution for: In (d) and Sn (e).

As shown in this Figure, the use of the PC led to a more homogeneous and compact deposit as compared to direct current conditions with a slight decrease of the particles size up to 1–1.2 μm. Moreover, as illustrated by EDX maps, the alloying elements are uniformly distributed in the coating.

Figure 4 presents the dependence of the indium content in the deposit against the applied average current density under PC conditions.

Figure 4. Dependence of the indium content in In–Sn alloy deposits vs. average applied current density from 100 mM InCl₃ + 50 mM SnCl₂, at 60 °C under pulsed current (PC) conditions, $t_{on} = t_{off} = 50$ ms.

A relatively linear decrease of the indium percentage with the current density increase was noticed, in a quite similar manner evidenced under direct current electrodeposition conditions. However both the range of indium content and of the current density were larger when PC was used.

XRD analysis was applied to get information on the present phases in the electrodeposited In-Sn alloy films. Figure 5 presents a typical X-ray pattern of the In-Sn alloy obtained involving an ILEG-SnIn electrolyte containing 50 mM InCl_3 + 50 mM SnCl_2 .

Figure 5. X-ray diffraction (XRD) patterns of Sn-In alloy coating electrodeposited from ILEG based system containing 50 mM InCl_3 + 50 mM SnCl_2 , at 60 °C and 2.5 $\text{mA}\cdot\text{cm}^{-2}$. Inset: the enlargement of the region corresponding to 2θ between 60° and 100°.

The presence of InSn_4 phase (with characteristic peaks at 29.76°, 32.1°, 44.34°, 57.23°, 61.83°, 65.85°, 71.39°, 79.92°) and In_3Sn phase (characteristic peaks at 2θ 32.83°, 36.52°, 41.29°, 56.23°, 63.34°) was identified, with some Sn traces.

As Figure 5 shows, the diffraction peaks which are associated with (001), (100) and (101) diffraction planes of hexagonal InSn_4 (PDF Card No. 01-077-2746) are the most intense. In addition, diffraction peaks corresponding to (101), (110) and (002) planes with smaller intensities corresponding to tetragonal In_3Sn (PDF Card No. 01-077-2749) were also detected, along with some peaks of the Sn traces and Cu substrate.

It is worth mentioning that the phase composition of the Sn-In alloy coatings remained the same for the investigated electrodeposition conditions.

Quite similar XRD patterns were reported in [38,39] for In-Sn alloy layers electrodeposited in $\text{EMI-BF}_4\text{-Cl}$ melts.

TGA analysis was used to get information on the melting point of the electrodeposited In-Sn alloys. Figure 6 illustrates examples of the recorded TGA curves for different In-Sn alloys electrodeposited both under direct current and PC conditions. The electrodeposition was carried out on Ti substrate that further allowed the easy detaching of the alloy.

Figure 6. Thermogravimetric analysis (TGA) for In–Sn alloy electrodeposited from ILEG–InSn electrolyte containing: (a) 100 mM InCl_3 + 30 mM SnCl_2 , $3 \text{ mA}\cdot\text{cm}^{-2}$ (direct current, Ti substrate) and (b) 50 mM InCl_3 + 50 mM SnCl_2 , $20 \text{ mA}\cdot\text{cm}^{-2}$ (pulsed current, Ti substrate).

As shown in Figure 6, melting temperatures of 127.5°C and of 118.6°C were determined quite close to the values corresponding to 50In–50Sn and to 52In–48Sn lead free solders [48].

3.2. Solderability Tests

To obtain preliminary information on the reliability of the In–Sn alloys as solder joints the applied procedure followed the steps according to [41,42]. Consequently, the pre-coated with In–Sn alloy specimens were subjected to immersion in molten SAC 305 alloy for 10 s at 245°C . After dipping in solder bath, the specimen surface was assessed visually for evidence of the non-wetting and de-wetting areas. In addition, the wetting angle was determined, which is an indicator of the degree of solder contact and strength of the solder joint.

Figure 7 presents images of the wetting angle formed between the SAC 305 alloy and In–Sn alloy coating after reflow at 245°C as well as of the sample surface mounted printed circuit boards (PCBs) and microsection through the solder joint on the PCB pre-coated with Sn–In alloy.

Figure 7. (a) Optical micrograph of the prepared microsection for the measurement of the wetting angle formed between the SAC 305 alloy and In–Sn alloy coating after reflow at 245°C ; (b) images of the sample surface mounted PCBs and microsection through the solder joint on the PCB pre-coated with Sn–In alloy.

As exemplified in this figure, wetting angles around 27° were determined, less than 90° , suggesting proper solderability characteristics. However, the visual examination evidenced the presence of some nonwetting and dewetting areas which might be due to the possible presence of oxides on the alloy surface before immersion in the molten SAC alloy.

As shown in Figure 7b, the solder joints showed a proper adhesion to the substrate with no fractures. These findings suggest that the Sn–In alloy coatings ensure a suitable bonding with the solder paste material.

3.3. Corrosion Behavior of Sn–In Alloy Coatings Obtained from Deep Eutectic Solvents (DESs)

Potentiodynamic polarization curves (not shown here) and electrochemical impedance spectra (EIS) at open circuit potential, in a free-aerated 0.5 M NaCl aqueous solution at room temperature, after different immersion periods were recorded to obtain information on the corrosion performance of the obtained Sn–In alloys coatings.

The EIS spectra of Sn–In alloy coatings recorded at open circuit potential (OCP) in 0.5 M NaCl solution for different immersion periods are shown in Figure 8, as Nyquist and Bode plots. The equivalent circuit to describe corrosion behavior of Sn–In alloy deposits in the NaCl solution is shown in Figure 8c.

Figure 8. Nyquist (a) and Bode (b) plots for Sn–In alloy coating in 0.5 M NaCl at open circuit potential, after various continuous immersion periods (solid lines are the fit of the measured points using the equivalent circuit shown in (c)).

All Nyquist diagrams show a semi-circle arc in the relative high-frequency range. The semicircles continue in low frequencies with almost linear portion indicating the formation of an adherent layer of corrosion products. The diameter of the semicircles is associated with the polarization resistance (charge transfer resistance, R_{ct}) which may be correlated to the rate of corrosion: the larger the resistance, the lower the corrosion current. All Bode diagrams indicate a single time constant for corrosion kinetics, with the maximum modulus of impedance ($|Z|$) at lowest frequencies having values of ca 10,000–30,000 Ω . Also, the maximum of the phase angle curves is recorded at 10–30 Hz frequency. It started from -75° , decreased suddenly to -67° after 24 h immersion and then increased (in 24–216 h period) and decreased (in 216–360 h period) within this range of values.

The process can be modeled as an ohmic resistance of solution (R_{sol}) in series with a parallel circuit consisting in a double-layer capacitor (C_{dl}) and a charge-transfer resistor (R_{ct}). During the fitting of the experimental data a constant phase element (CPE) was used instead of true capacitance (C_{dl}) [49], in order to model more accurately the non-ideal behavior of C_{dl} capacitance.

In Table 2 the resulting values of the charge-transfer resistance (R_{ct}) for the corrosion of Sn–In alloy are presented, which were obtained by fitting the impedance data with ZView software. It can be seen that R_{ct} decreased from an initial value of about 32.8 k Ω towards 7.6 k Ω after 144 h of conditioning. The semicircle diameter (which corresponds to R_{ct}) decreased faster in time in the first 24 h period

indicating an intense corrosion, probably due to the activation of some defects. During the period 24–144 h this decrease of R_{ct} was slowed down due to formation of a less porous layer that still allows Cl^- ions penetration to Sn–In alloy surface.

Table 2. Values of R_{CT} by fitting impedance results for Sn–In alloy coating after exposure to 0.5 M NaCl solution for different times using the equivalent circuit proposed in Figure 8c.

Immersion Time/h	R_{ct}/Ω
0	32,807
24	8715
144	7658
216	14,290
360	34,607

It follows a corrosion step (144–360 h) when R_{ct} increased, indicating the thickening the layer of corrosion products on the Sn–In surface, so that it may act as a passive layer, with protective behavior restored.

4. Conclusions

As a result of the investigations performed, several electrochemical procedures to prepare adherent and uniform Sn–In alloys containing 10–65 wt.% In from choline chloride-ethylene glycol eutectic mixtures were proposed. The In content was found to increase as both the In:Sn molar concentration ratio of ionic species in the electrolyte and the applied temperature increased.

SEM micrographs of the electrodeposited alloy coatings evidenced the presence of quite irregular particles entirely covering the metallic substrate under direct current plating conditions, while a more homogeneous and compact deposit, with a slight decrease of the particles size, was obtained using PC. In addition, the pulsed current procedure allowed the use of higher current densities leading to slightly higher values of In content in the alloy deposit.

The XRD analysis revealed the presence of $InSn_4$ and In_3Sn phases in agreement with the phase diagram. According to the TGA measurements, melting points in the range of 118.6 and 127.5 °C were obtained, depending on the alloy composition.

The obtained results showed adequate solderability performance and a good corrosion performance. After 360 h of continuous immersion in chloride containing aggressive medium, the exposed specimens did not exhibit any major surface modification.

While this study showed that the electrodeposition of Sn–In alloy coatings from DESs is possible, more investigations are needed to gain a better understanding of this alloy deposition mechanism with direct impact on its composition and application in various domains, including electronic industry. The results of this study will be presented in a separate manuscript.

Author Contributions: Conceptualization, writing-original draft preparation, corrosion experiments and analysis L.A.; electrodeposition methodology and experiments, analysis A.P.; electrodeposition experiments, solderability methodology, testing and analysis, S.C.; TGA measurements and analysis, C.M.; SEM, XRD. investigation and analysis, O.B.; writing—review and editing, visualization, T.V.

Funding: This research work was funded by Romanian Ministry of Education and by Executive Agency for Higher Education, Research, Development and Innovation Funding, under NOVTINALBEST project 38/2016, M Era Net Program and under ROFCC project, Contract No. 25 PCCDI/2018.

Acknowledgments: The authors would like to thank to M. Enachescu for technical support and assistance in the films characterization (SEM, XRD, TGA).

Conflicts of Interest: The authors declare no conflict of interest.

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