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Co-electrodeposition of tin with 0.2–20% indium: Implications on tin whisker growth

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ABSTRACT

The growth of whiskers on tin-plated interconnects causes acute short circuit problems and system failures in electronic components. In the past, this problem was suppressed by the addition of a few percent Pb in the electroplated tin, but following the introduction of international laws restricting the use of lead in electronics, alternative strategies are necessary. Recently it has been shown that 5–10% indium can eliminate whisker growth in electroplated tin on copper substrates under ambient temperature aging. However, there is no currently known method for co-electrodepositing Sn with a small amount of In using an acidic electrolyte that is similar to that currently used in the industry. This paper reports on a method to co-electroplate tin with 0.2 to 20 atomic percent indium from a methanesulfonic acid (MSA) electrolyte, which is the most widely used bath for electroplating of Sn, with only a small amount of other additives. The impact of co-deposited Sn-In platings on the susceptibility to whisker growth has been demonstrated.

1. Introduction

Tin whiskers have caused serious reliability problems particularly in long-life electronic applications. There have been numerous instances of failure in space [1,2], defense [3–5], transportation [4,5] and medical-implant industries [6,7]. Some of them have been documented on the NASA tin whisker website [1,2]. The tin whisker problem became more acute, following passage of the European Union directive in 2006 [8], which restricted the use of Pb in electronics, because Pb was used as an alloying element for suppressing tin whisker growth in the past [6]. Hence, various substitute approaches that mitigate, but not eliminate whisker growth of Sn, are currently used. These include using Bi [9,11,14], Ni underlayer [11,12], conformal coatings [10,13], etc.

Recently it has been shown that 5–10% Indium can eliminate whisker growth in electroplated tin on copper substrates under ambient temperature aging [15–19]. As such, in terms of Sn whisker mitigation, indium is an even better additive than Pb. However, there is no currently known method for co-electrodepositing Sn with a small amount of In using an acidic electrolyte that is similar to that currently used in the industry.

The difficulty in co-plating Sn and In is primarily associated with the large difference in the standard electrode potentials of the Sn/Sn^{+2} and In/In^{+3} half-cells, which are -0.141 V and -0.338 V relative to the standard hydrogen electrode, respectively [20]. This leads to the deposition of Sn only, precluding simultaneous deposition of In. The only approaches by which Sn and In have been co-plated to date include harsh alkalis or acids in the plating bath, and yield relatively large amounts of In within the plating (close to 50 atomic %). These methods are outlined below, along with their limitations for widespread practical usage. Sn-In co-plating has been conducted using Sn^{4+} or Sn^{2+} ions in either an acidic bath (citric, tartaric or acetic acids) or an alkaline bath (potassium tartarate), with both baths containing alkaline salts of carboxylic acid as chelating agents that slow down Sn deposition [21]. Between the two baths, the alkaline bath was better in terms of stability and control of the plating process, because the acidic bath had a very narrow process-window, making plating difficult. However, there is a strong preference for acidic baths in the Sn-plating industry, and as such, neither process in [21] is suitable for industrial use. In a different study [22], four kinds of baths, i.e., fluoborate, chloride, sulfate and cyanide, were studied for the electro-deposition of Sn-In alloys. Of these, only the cyanide bath, which is strongly alkaline (pH $>$ 12), produced good coatings. However, the high toxicity of cyanides makes this approach unattractive for large-scale industrial use. Similar to [21], stability and current efficiency of the cyanide plating bath were improved by adding Rochelle salt, an alkaline salt of carboxylic acid. A cyanide-free Sn-In alloy electroplating solution using indium salts of an organosulfonic acid (e.g., methanesulfonic acid or MSA) and an acidic tin salt (a salt of metastannic acid) has been reported in [23], but the plating bath was titrated with sodium hydroxide to an alkaline pH between 7 and 11. Thus, all of the above approaches for

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electrodeposition of Sn-In alloys that are robust utilize alkaline baths, which is not attractive from the standpoint of industrial application.

In a recent Russian patent [24], an acidic bath comprising tin sulfate, indium sulfate and sulfuric acid has been used for co-electroplating tin-indium alloy, in which the indium content ranges from 0.5 to 56 wt %. In another work, Russian scientists [25] reported on using an acidic sulfate electrolyte bath for electrodeposition of tin-indium alloy in the presence of organic additives like synthanol, formalin and butynediol. Although these approaches [24,25] use acidic baths based on sulfuric acid, to date, there has been no report on co-electrodeposition of Sn and In using a methanesulfonic acid (MSA) based bath, which is currently the most widely-used commercial bath for Sn deposition [e.g., 7,26,27], and has also been used for In deposition [28,29]. MSA is an attractive electrolyte primarily because of four reasons [30]: (i) the aqueous solubility of metal methanesulfonates, (ii) the high conductivity of aqueous solutions of MSA, (iii) the low toxicity of MSA, and (iv) the environmental friendliness of the aqueous process effluent treatment, acid recovery, and metal alkanesulfonate salt formation.

The purpose of this study is to establish a methodology to co-electrodeposit Sn with 0.2 to 20 atomic percent In, using an electrolyte based on MSA, and widely available, inexpensive tin and indium salts and commonly used additives. The objective is to produce a method for co-plating Sn and In over wide range of compositions, ranging from Sn doped with a small amount of In at one end, to Sn-In solders with an appreciable amount of In (e.g., 20%) at the other end, with minimal modifications to industrially used approaches based on MSA baths.

This study reports on a method to co-electroplate Sn with 0.2 to 20 atomic percent In from a methanesulfonic acid (MSA) electrolyte, which is the most widely used bath for electroplating of Sn, with only a small amount of other additives. The impact of co-deposited Sn-In platings on the susceptibility to whisker growth is also demonstrated.

2. Experimental procedure

2.1. Preparation of the electrolyte

Electroplating baths with two different compositions were prepared for co-deposition of tin with nominally 10 at.% and 5 at.% indium. They were named as electrolyte 1 and electrolyte 2 respectively. These two electrolytes were prepared from salts of divalent tin and trivalent indium ($SnSO_4$, $In_2(SO_4)_3$), methanesulfonic acid, a chelating agent (gluconic acid, $C_6H_{12}O_7$), and a pH adjustor (NaOH) as essential components, and an antioxidant (hydroquinone, $C_6H_6O_2$), a grain refining additive (porcine gelatin), and a hydrogen suppressor (poly-ethylene glycol, PEG) as optional components, in deionized water.

The preparation process of electrolyte 1 is described below. First, 30 g of tin sulfate (Sn^{2+}) and 5 g of indium sulfate (In^{3+}) was added in 1 l of deionized (DI) water and stirred continuously until it formed a uniform mixture, i.e., there was no settlement of these compounds at the bottom of the beaker. Then, 60 g of methanesulfonic acid was added to the plating bath followed by the addition of 70 g of gluconic acid. Methane sulfonic acid (MSA) was used as the electrolyte, because it is the industrial standard in commercial plating baths for Sn. The purpose of using MSA was to increase the conductivity of the plating bath.

Gluconic acid was used as the chelating agent in the plating bath. A chelating agent is a substance whose molecules can form several bonds to a single metal ion. Gluconic acid forms chelate bonds with tin and reduces the mobility of tin ions, which ensures the deposition of tin and indium at a desired ratio. Then, 5 g of hydroquinone (HQ) was introduced into the plating bath to prevent the spontaneous oxidation of Sn^{2+} to Sn^{4+}. HQ functions as an antioxidant by removing the dissolved oxygen and suppresses hydrogen evolution.

Subsequently, the plating bath was stirred and 0.2 g of gelatin was added to it. The purpose of adding gelatin was that it functioned as a levelling and grain refining agent. The morphology of the electroplated films became smoother on adding gelatin. Optionally, 10 g of polyethylene glycol (PEG) was added to the electrolyte to suppress hydrogen gas evolution during Sn-In deposition. PEG functioned as a hydrogen suppressor by lowering the potential (i.e., driving it in the cathodic direction), which allowed deposition of the metal without the simultaneous evolution of hydrogen gas. This increased the current efficiency at the cathode and enabled the formation of uniform deposits. The pH of the resulting electrolyte was measured using a pH meter and was found to be highly acidic (pH ~ 0.1). Therefore, as a final step, sodium hydroxide was introduced into the plating electrolyte, in desired amount, to adjust the pH to a value of ~1.2.

Table 1
Constituents of electrolyte 1 and electrolyte 2 (in g/l).

Name of constituent	Electrolyte 1 composition (g/l)	Electrolyte 2 composition (g/l)
Tin sulfate	30	30
Indium sulfate	5	2
Methanesulfonic acid	60	60
Gluconic acid	70	70
Hydroquinone	5	5
Gelatin	0.2	0.2
Polyethylene glycol	10	10

Electrolyte 2 was prepared in a similar fashion as electrolyte 1, but by varying the amounts of specific components. 30 g of tin sulfate (Sn^{2+}) and 2 g of indium sulfate (In^{3+}) was added in one liter of deionized (DI) water followed by the addition of 60 g of methanesulfonic acid, 70 g of gluconic acid. The solution was stirred, and then 5 g of hydroquinone, 0.2 g of gelatin and 10 g of polyethylene glycol were added to it progressively. Finally, sodium hydroxide was added in desired amount (to adjust the pH to ~1.3). The functionality of the various components added to the electrolyte has been described in the previous paragraph. Table 1 lists the constituents of both electrolyte 1 and electrolyte 2.

2.2. Co-deposition process

Co-deposition was conducted on oxygen-free high-conductivity (OFHC, 99.99% Cu) copper plates, with dimensions of 2.5 cm × 2.5 cm × 1 mm. The copper plates were metallographically polished with silicon carbide (SiC) paper, diamond suspensions and a mildly basic (pH ~ 11) colloidal silica solution until a mirror finish was obtained. Further details of the sample preparation process can be found in [15,17]. The copper substrate served as the cathode, while F-304 stainless steel was used as the anode material. The anode-to-cathode distance was approximately 6 cm. The co-deposition was conducted at room temperature (RT), using a current density of 20 mA/cm^2. Approximately 1 l of electrolyte was placed in a cylindrical tank with a capacity of 1.5 l, and the electrolyte was stirred at approximately 300 rpm using a magnetic stirrer to facilitate uniform film deposition. After plating, the samples were rinsed in de-ionized water and dried in air. Multiple samples were prepared by co-deposition from electrolyte 1 and 2, and the plating rate was determined to be ~0.75 μm in 1 min. The deposited Sn-In films had a nominal thickness of 3 μm. Two and four samples each were prepared for electrolytes 1 and 2, respectively. Half of each type of samples made was analyzed quantitatively for whisker growth kinetics.

2.3. Characterization, heat treatment and analysis

The deposited layer thicknesses were measured with white light interferometry (ZYGO NewView 6300). Energy dispersive spectroscopy (EDS) was utilized to assess the compositions of the two different coatings (nominally 10 at.% and 5 at.% In) produced. Following analysis of the film thickness and composition, a set of Sn-5%In samples were heat treated at 160 °C for four hours in high vacuum (pressure of