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Effect of additives on the co-electrodeposition of Sn–Ag–Cu lead-free solder composition

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ABSTRACT

We have developed a methane sulfonic acid (MSA) based ternary electrodeposition bath for the deposition of near eutectic Sn–Ag–Cu films aimed at solder bumping applications in electronics. The bath contains thiourea as chelating agent and *iso*-octyl phenoxy ethanol (OPPE) as surfactant. We added gelatin to this bath and studied its effect on bath stability, microstructure of the deposited films and the film composition. It is found that the bath containing both the additives, *viz.* OPPE and gelatin, show improved stability up to 8–10 days. Striking improvement in the film microstructure, in terms of the compactness, uniformity and refinement of grains was found when the bath contained these additives. Detailed electrochemical studies with the help of cyclic voltametry and impedance analysis helped in understanding the role played by these additives during deposition. It is confirmed that there is a formation of loosely connected, highly non-uniform passivating film on the cathode surface, which is removed competitively by the depositing metal ions during the deposition. It is also clear that the additives play a role in the formation of such a passivating film.

1. Introduction

Recently, electrodeposition of solder alloys has generated renewed interest in electronics, mainly due to its ability to deposit solders selectively and uniformly at micron scale. One important use of such electrodepositions in electronics is solder bumping. Today, 100 μm size electrodeposited solder bumps at 250 μm pitch are in commercial use and lower dimensions are reported at research level [1,2]. Simultaneous with these developments, the environmental concerns due to Pb contained in solders have underlined the need for lead-free solder in the recent years. Amongst the contending binary and ternary lead-free alloys which are under investigations, the eutectic composition of Sn–Ag–Cu, *viz.* Sn–3.5Ag–0.8Cu, is amongst the forerunners for the potential replacement of lead containing solder alloys. This eutectic alloy has a melting point of 217 °C, which is lower than the melting point of binary Sn–Ag or Sn–Cu eutectic alloys. Apart from this, most of the physical and mechanical properties of this ternary alloy are comparable to the Sn–Pb eutectic, which makes it one of the most favored choices [3].

While it is possible to deposit solder components sequentially and obtain the desired solder alloys after reflow, in practice it is difficult to control the alloy composition precisely using this method, especially when the composition contains vary small amounts of individual metal. This difficulty has been partially circumvented using sequential deposition of binary alloys. There are reports of sequential deposition of binary Sn–Ag and Sn–Cu films to obtain the desired ternary composition [4]. However, this method is still cumbersome due to the need for multiple depositions in different baths that finally adds to the issues of reliability and repeatability. On the other hand, co-deposition of the three solder components would, in principle, help in precise composition control across the micron-size depositions. However, such co-deposition of a multi-element system has its own difficulties. An ideal co-deposition bath should deposit all the elements at a single or in a narrow range of potential. This is rare, and is certainly not true for the Sn–Ag–Cu system. It is necessary to add appropriate chelating agents to bring the deposition potentials closer. The other additives also play a very crucial role in co-deposition baths. While chelating agents alter the deposition potentials, the additives function as grain refiners, surfactants and surface-active agents and help in obtaining a stable bath with consistent properties. As grain refiners they adhere to the deposited films, force the creation of fresh nuclei and refine the film microstructure. Improvement in film microstructure is also obtained through the use of surfactants and surface-active agents. In practice, selection of appropriate additives for such varying functions in the bath depends on the type of bath system, the different bath constituents and other parameters, such as, pH and deposition temperature.

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There are few reports on electrodeposition of ternary Sn–Ag–Cu systems. Amongst the reported baths, sulfuric acid and MSA based electrolytes are most common. The sulfuric acid based baths are cheap and show good results, however, their corrosive nature is a major issue. Comparatively MSA based baths are environmentally friendly and much safer to work with. Further, most of the metal salts have good solubility in MSA. This bath can be used to deposit good quality films even at higher current densities that may range up to 2000 mA cm^{-1}. Its ability to control the oxidation of $Sn^{2+}$to Sn^{4+} is its most important advantage [5].

We have developed a MSA based co-deposition bath for Sn–Ag–Cu alloys using thiourea as chelating agent and a commercial surfactant, *viz. iso*-octyl phenoxy ethanol (OPPE) as an additive [6]. Thiourea is seen as the most appropriate chelating agent since it is known to form chelates with both silver and copper [7,8]. However, its effectiveness in chelating both the ions in a co-deposition bath was required to be investigated. Our investigations show that thiourea does form chelates with both copper and silver ions in the MSA based co-deposition systems [6]. It was also found that addition of OPPE to this thiourea containing ternary system causes further improvement in the bath stability and microstructure. The OPPE molecule links with metal ions through the oxygen atom and helps in forming a protective coating around the suspended material, in-turn prohibiting their mutual interaction in liquid phase [9]. This may be responsible for preventing their reduction in the electrolyte bath. However, this bath needed further improvement as it was found to be stable for just about 4–5 days. Gelatin, which is a surface-finishing agent, is known to alter the viscosity of the electrolyte that reportedly enhances the bath stability and microstructure of the deposited film [10]. We added gelatin to the OPPE and thiourea containing bath and found similar improvement in the results. In this work we have studied the combined effect of OPPE and gelatin in obtaining a stable co-deposition bath for Sn–Ag–Cu system through its comparison with a bath without these additives. We have carried out cyclic voltametry and impedance analysis of baths with and without additives and examined the microstructure and elemental composition of the deposited films. A glimpse of the deposition process is thereby obtained.

2. Experimental

2.1. Materials

Laboratory reagent (LR) grade methane sulfonic acid, copper sulfate, thiourea and *iso*-octyl phenoxy ethanol (OPPE) were purchased from Loba Chemie (Pvt) Ltd., Mumbai, India.

Tin–methane sulfonate was purchased from Sigma–Aldrich Chemie, Germany. LR grade silver sulfate and gelatin were purchased from Qualigens fine chemicals, Mumbai, India.

2.2. Preparation of plating baths

The MSA based ternary Sn–Ag–Cu bath, which is developed in-house, uses tin methane sulfonate as a source of Sn ions while the Cu^{2+} and Ag^{+} ions were obtained from their respective sulfate salts. Thiourea and *iso*-octyl phenoxy ethanol (OPPE) served as chelating agent and surfactant respectively. The bath also contained gelatin, which helped in improving the bath properties further. Multiple baths (OP1–OP3) with different combinations of these additives were formulated for this study as follows.

For the preparation of all plating baths, a master batch of MSA solution in water containing thiourea was prepared. Also the acetate salts of sodium and ammonium were used as buffers to raise the pH of the plating baths.

Table 1
Chemical composition of ternary Sn–Ag–Cu Co-deposition baths studied.

S. No.	Chemical	Composition		
		OP1	OP2	OP3
1	Methane sulfonic acid	1.54 M	1.54 M	1.54 M
2	Tin methane sulfonate	0.34 M	0.34 M	0.34 M
3	Copper sulfate	0.08 mM	0.08 mM	0.08 mM
4	Silver sulfate	1.2 mM	1.2 mM	1.2 mM
5	Thiourea	0.04 M	0.04 M	0.04 M
6	OPPE	12 g/lit	–	12 g/lit
7	Gelatin	2 g/L	–	–

2.2.1. Plating bath OP1

To prepare plating bath OP1, about 1.2 mL of OPPE was added to 100 mL of MSA solution in water containing thiourea. To this solution, predetermined quantity of tin methane sulfonate, copper sulfate and silver sulfate were added sequentially at room temperature in beaker, while stirring using magnetic stirrer. Subsequently, gelatin was added to the bath while continuing stirring. This was followed by the addition of the buffer salts, and the pH of the solution was raised to pH 4. Continuous stirring was done to ensure complete solubility.

The detailed chemical composition of the OP1 bath is given in Table 1.

2.2.2. Plating bath OP2

To prepare plating bath OP2, tin methane sulfonate, copper sulfate and silver sulfate were added sequentially to 100 mL of MSA solution in water containing thiourea at room temperature in beaker, while stirring using magnetic stirrer. This was followed by the addition of the buffer salts, and the PH of the solution was raised to pH 4. Continuous stirring was done to ensure complete solubility. The detailed chemical composition of the OP2 bath is given in Table 1.

2.2.3. Plating bath OP3

To prepare plating bath OP3, about 1.2 mL of OPPE was added to 100 mL of MSA solution in water containing thiourea. To this solution, predetermined quantity of tin methane sulfonate, copper sulfate and silver sulfate were added sequentially at room temperature in beaker, while stirring using magnetic stirrer. This was followed by the addition of the buffer salts, and the pH of the solution was raised to pH 4. The detailed chemical composition of the OP3 bath is given in Table 1.

2.3. Procedure for electrodeposition of film of Sn–Ag–Cu solders

The electrodeposition of Sn–Ag–Cu solder films were done using chronopotentiometry (galvanostatic) method of the potentiostat–galvanostat. Before deposition, the substrates were thoroughly cleaned with soap water, rinsed, dried and degreased using trichloroethylene.

For all the electrodepositions, Nickel coated (5 μm thick) copper clad substrates were used as cathode, and a Sn electrode served as anode during the electrodepositions process. The Ni film underneath solder helped in masking Cu signal emanating from the Cu clad substrate during EDS analysis. This Ni film was electodeposited using a commercial Ni plating bath (Spectra 77, M/s Grauer and Weil (I) Ltd., India) at 55 °C at current density of 40 mA cm^{-1} for 7 min to obtain about 5 μm thick film.

A deposition area of 1 cm^2 was defined by masking the substrate using adhesive tapes. All the depositions were carried out at room temperature for duration of 1 h at a current density of 10 mA cm^{-1}. After deposition the films were rinsed in water, dried and characterized for microstructure and elemental analysis.