Chapter 1 - Introduction

1. Introduction

1.1 Background

In the electronic packaging industries soldering materials are essential in joining various microelectronic networks (Abtew and Selvaduray, 2000). Solders assure the reliability of joints and protect the microelectronic packaging devices. They provide electrical, thermal and mechanical continuity among various interconnections in an electronic device (Abtew and Selvaduray, 2000; Suganuma, 2004). Lead containing solders are in use for years resulting in an extensive database for the reliability of these materials (Tu and Zeng, 2001). The service performance of all the electronic appliances depends on high strength and durable soldering materials.

1.2 Environment concerns

Through history it is already known that in the electronic packaging devices, the most common solder is Sn-Pb. However, with rise of electronic market, there is a hot issue over the toxicity of Pb among the electronic manufacturers. In the last few decades, the effect of lead contamination on human health has received significant attention. Leaching of this toxic lead from electronic wastes results in contamination of the human food chain and causes serious health hazards. The toxic fumes on burning these wastes can cause lung cancer and affect the nervous system, reproductive systems, kidney and cardiovascular organs over prolonged exposure and may eventually lead to death (Puttlitz and Stalter, 2004). Every year, lead is accumulated in our landfills through our used and waste domestic appliances. If one such unit contains 10 g lead, it can be shown that total lead accumulated per year becomes about 200 ton, which is definitely a huge amount. As a consequence, several European Union countries have passed legislations that impose elimination of lead from electronic solders (Suganuma, 2004; Puttlitz and Stalter, 2004). In view of these serious environmental health problems and legislations, the scientific community across the world have started to ban the use of Pb in their electronic assemblies. These activities have fuelled an extensive research in the electronic manufacturers to find promising lead free solders all over the world. Besides the environmental issue, use of lead in electronic devices also poses a radioactive threat over prolonged use. These radioactive Pb generates α-particles during its decay causing failure of memory chips. This is often called soft errors in electronic memory devices (Heijmen, 2002; Seifert *et al.,* 2001; Tu e*t al*., 2003). Therefore, not only strict control but almost a complete removal of Pb in high capacity memory goods is necessary.

1.3 Current Scenario

There is tremendous research going on to search for a better lead free solder alloy but still none has replaced completely the traditional Sn-Pb solder in terms of performance, ease of manufacture, cost, availability, wetting characteristics, mechanical strength, and intermetallic compound formation (Coombs, 2001; Subramanian, 2007).

In the present state the advanced solders that have been developed so far are mostly Sn rich alloys containing Cu, Ag, Zn, Bi, Sb, Ni etc. (Guo, 2006; Alam *et al.*, 2009; Lai and Duh, 2003; El-Daly and Hammad, 2010; Miao and Duh, 2001; Nogita and Nishimura, 2008; Lin and Shih, 2008). Among all the binary eutectic Pb-free alloys, SnAg, SnZn and SnCu are considered to be the potential candidates to replace Sn-Pb. As for ternary alloys, those in the SnAgCu system is considered promising due to its lower melting temperature and superior mechanical properties compared to the binary compositions (Wu *et al.*, 2004). However, there are some issues of reliability problems over long term use such as formation of large and brittle intermetallics of Ag_3Sn and Cu_6Sn_5 in ternary alloys which may have negative effect on mechanical properties (Suganuma, 2001).

Though these lead free Sn rich alloys are perfect replacement for lead based solders, their mechanical properties make their durability less than satisfactory. Moreover, these Sn rich alloys are prone to whisker growth with ageing causing short circuiting in electronic devices and ultimate failure. The driving force for Sn whisker formation is believed to be the internal stresses caused by the volume expansion due to the formation of intermetallic compounds like Cu_6Sn_5, Cu_3Sn etc with time (Suganuma, 2004).

To meet the requirement, lead free solder alloys must be developed that are not only having superior strength but also have a minimum tendency of whisker growth. Recently, research activities are aimed at the development of solder alloys reinforced with nanoceramic particles in order to achieve the desired properties. Such reinforced solder alloys are known as nano-composite solders. Composite solders are more reliable because the reinforcing particles can suppress grain-boundary sliding, refine the intermetallic compound (IMC), suppress grain growth, and redistribute the stress uniformly (Shen and Chan, 2009; Guo 2006). This new modern approach to develop these solders would provide higher strength and reliability of solder joints. Researchers have been working on their development in order to achieve a better combined properties (Shen and Chan, 2009; Jin and McCormack, 1994).

Various synthesis routes like metal casting route, powder metallurgy, mechanical alloying, physical vapour deposition, sol-gel, plasma sprayed deposition, chemical reduction method, electrodeposition etc. have been used to produce solder materials (Miller, *et al.*, 1994; Alam *et al.*, 2009; Lai and Duh, 2003;; Aggarwal *et al.*, 2007; Conway *et al.*, 2002; Hsiao and Duh, 2005; Hsiung *et al.*, 2007; Ruythooren *et al.*, 2000). Among all these routes, electrodeposition is the most versatile method for producing these solders in coating form, bulk form and as composites (Bicelli et. al., 2008; Hovestad and Janssen, 1995).

Most of the solder matrix composites are reinforced with ceramic particles like Al_2O_3, ZrO_2, SiC, TiO_2, Cu_2O, SnO_2 etc. (Zhong and Gupta, 2008; Shen *et al.*, 2006; Liu *et al.*, 2008; Tsao and Chang, 2010; Sivasubhramaniyam *et al.*, 2008; Babaghorbani *et al.*, 2009a; Abtew and Selvaduray, 2000; Shen and Chan, 2009). However, there is a limited research on co-electrodeposited solders. Some studies on Sn based nanocomposite solders are already reported for the Sn-CNT and SnBi-SiC systems (Choi *et al.*, 2008; Shin *et al.*, 2009). It can be found in the literature that CeO_2 has been rarely used for reinforcing the solder matrix by electrodeposition process inspite of its attractive properties. It possess high strength, high wear and corrosion resistance and highly inert towards acids and bases. Ceria based ceramics are in demand because of their higher ionic conductivity than zirconia for the same solute concentration (Aruna *et al.*, 2006). Ceria base catalysts are in use in gas sensors, electrodes in SOFC, high temperature coating for oxidation prevention (Zhitomirsky and Petric, 2001). Well dispersed nanosized ceramic particles in a metal matrix can significantly improve the mechanical strength, and wear and corrosion resistance of the matrix without sacrificing significantly the electrical and thermal properties [Mangam, (2010, 2011)]. Therefore, it opens up potential applications of the Sn based nanocomposite solder materials in microdevices.

1.4 Objectives

The specific objectives of the present investigation are

- To synthesize pure Sn coatings by pulse electrodeposition technique from different aqueous solutions.
- To study the effect of the pulse electrodeposition parameters (e.g., current density, additive concentration, duty cycle, frequency, pH, temperature, and stirring rate) on the morphology of pure Sn coatings.
- To synthesise the nanocrystalline CeO_2 by high energy ball milling method.
- To synthesize the Sn/CeO_2 and near eutectic Sn-Ag/CeO_2 composite films with varying amount of CeO_2 and their subsequent microstructural characterization.
- To evaluate the microhardness, density, porosity, melting behavior, wear and friction characteristics, corrosion behavior, electrical resistivity, and residual stress of the developed composites.

1.5 Contributions

(1) An optimized set of parameters have been developed to obtain desired morphology and grain size distribution of the coatings. The optimized parameters for pulse electrodeposition of tin from sulfate bath are current density = 0.2 A/cm^2, amount of additive (Triton X-100) = 0.2 g/L, duty cycle = 10%, frequency = 100 Hz, pH = 1, bath temperature = 28 ^{o}C, and stirring rate = 300 rpm.

(2) It has been shown that the Sn/CeO_2 and Sn-Ag/CeO_2 nanocomposites can be synthesized using pulse co-electrodeposition method and an incorporation of CeO_2 in the Sn/(Sn-Ag) matrix leads to a significant increase in microhardness, wear and corrosion resistance and minimises the chances for whisker growth.

(3) This study proposes the incorporation of an optimum amount of ceria in the Sn based-ceria nanocomposites for the enhancement of various properties and thus improved coating life.

1.6 Research Plan and thesis outline

The whole thesis is devided into 5 chapters.
Chapter 1 gives a brief introduction about the background and the current scenario of the soldering materials.
Chapter 2 gives a detailed literature survey of the existing solders, next generation solders and the composite approach of soldering.
Chapter 3 gives the information about the materials synthesised, methodology used for the synthesis of monolithic and composite solders and their characterization, and property evaluation.
Chapter 4 presents and discusses the obtained results from the investigated experiments.
Chapter 5 summarises the findings and suggests future directions for the next generation research based on this work.