We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,300

Open access books available

172,000

International authors and editors

190M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Pulse Electrodeposition of Lead-Free Tin-Based Composites for Microelectronic Packaging

Ashutosh Sharma, Siddhartha Das and Karabi Das

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/62036>

Abstract

This chapter provides a detailed overview of the various Sn-based composites solders reinforced with ceramic nanoparticles. These solders are lead free in nature and are produced by various process like powder metallurgy, ball milling, casting as well as simple and economic pulse co-electrodeposition technique. In this chapter, various electrodeposited composite solders, their synthesis, characterization, and evaluation of various properties for microelectronic packaging applications, such as microstructure, microhardness, density and porosity, wear and friction, electrochemical corrosion, melting point, electrical resistivity, and residual stress of the monolithic Sn-based and (nano)composite solders have been presented and discussed. This chapter is divided into the following sections: such as introduction to microelectronic packaging, synthesis routes for solders and composites, various nanoreinforcement, and the mechanism of incorporation in solder matrix, the pulse co-electrodeposition technique, the various factors affecting composite deposition, and the improved properties of composite solders over monolithic solders for microelectronic packaging applications are also summarized here.

Keywords: Composite, lead free, plating, double layer, zeta potential

1. Introduction

1.1. Microelectronic packaging

Microelectronic packaging is a multidisciplinary branch of materials engineering that deals with the study of various interconnecting materials, electronic components packaging from chip level to final board level, for example, computers, cellphones, notebooks, laptops, and iPads. It also includes a method of joining various components to the respective substrates, as well as reducing their weight/volume for faster processing, multifunctionality, and portability.

In olden times, various wires and cables are used to connect the different components into an electric box. With the passage of time, printed circuit boards (PCB), or printed wire boards (PWB) invented near 1950s as a great revolution among electronics industries. Moreover, the invention of transistors and integrated circuits (ICs), analog-to-digital electronics in 1947 made luxurious life style of the common public. This technology of interconnecting various IC's and other electronic component devices like transistors, capacitors, inductors, and resistors within circuits over a PCB substrate to form a compact electronic device is known as microelectronic packaging.[1, 2] The common packages in a personal computer are shown below (Fig. 1).

Figure 1. Micropackaging assemblies inside a personal computer.

1.2. Microelectronic packaging materials

Since the civilization, the most commonly used solder is lead–tin (Sn–Pb) solder in electronic packaging. However, the toxicity of Pb is a serious concern among the electronic manufacturers. Pb containing solders are in use so far due to their indispensable properties. The effect of Pb contamination on human beings is a serious threat nowadays. Therefore, Pb and its compounds in electronic devices are now being restricted on account of the bans and regulation imposed by European organizations such as restriction of hazardous substances and waste electrical and electronic equipments.[3–5] It is also to be noted that, though Pb is cost effective, available in abundance, and provides no undesirable reaction with the substrate, yet it shows some technical problems like inferior bonding strength which is important for microjoining.[1–6] Therefore, composites solders are now being regarded as an alternative to conventional Sn–Pb solders and developed to resolve these concerns.

1.3. Lead free packaging materials

Large number of Pb-free solder alloys have been developed and studied where Sn is the major fraction. The most popular Pb-free alloy system candidates are narrated in detail in a review

paper in Ref. [7]. In the present state, the advanced solders that have been developed so far are mostly Sn coupled with other elements like Cu, Ag, Zn, Bi, Sb, Ni.[8–14] Among all the binary eutectic Pb-free alloys, Sn–Ag, Sn–Zn, and Sn–Cu are considered to be the potential candidates to replace Sn–Pb. For ternary alloys, the most commonly used system is Sn–Ag–Cu which is proved the most effective due to its lower melting temperature and superior mechanical properties compared to the other combinations.[15] However, there exist some issues of reliability such as the formation of brittle/needle type intermetallics of Ag_3Sn and Cu_6Sn_5 in ternary alloys which damages the mechanical and soldering properties.[5, 16] These Sn-rich alloys are sensitive to tin whisker growth if prolonged for a long time which is known to cause short circuiting in electronic devices. The major driving force for tin whisker growth is known to be the internal residual stresses due to the inherent compounds like Cu_6Sn_5 , Cu_3Sn with time.[5]

2. Synthesis of nanocomposites solders

Although enormous amount of research activities are being done all around the world for a better lead-free solder alloy, no solder alloy is able to completely replace the conventional Sn–Pb solder in terms of performance, economy, availability, solderability, simplicity, mechanical strength, and substrate reaction.[4, 17]

In current research scenario, the development of solder alloys reinforced with nanoceramic particles is being paid more attention toward designing a lead-free solder. Such reinforced solder alloys are generally termed as nanocomposite solders. Nanocomposite solders have shown excellent solderability and reliability. Most of the solder matrix composites are reinforced with ceramic particles like ZrO_2 , Al_2O_3 , TiO_2 , SiC, Cu_2O , SnO_2 , La_2O_3 . [7, 18, 19, 21–25] The reinforcing particles suppress growth of intermetallic compounds (IMC) and provide uniform stress distribution in the matrix.[8, 18, 19] This method of nanotechnology would provide high strength and reliable solders for microelectronic packaging devices.[18, 20]

Various processing routes like melting and casting, powder metallurgy, high-energy ball milling/mechanical alloying, physical vapor deposition, sol–gel, plasma sprayed deposition, chemical methods, and electroplating have been employed to produce solder materials.[9–10, 26–31] Powder metallurgy and mixing methods have been often used to fabricate the lead-free solders reinforced with nanoparticles: Cu, SiC, ZrO_2 , Al_2O_3 , SnO_2 , Y_2O_3 , TiB_2 , carbon nanotube (CNT), rare earth.[9, 21–22, 25, 32–36] There is also a limit on the amount of nanoreinforcement addition in the solder matrix; otherwise, it will deteriorate the solderability and strength. In literature, there is a limited research on solders produced by electrodeposition with a few studies on Sn–CNT and Sn–Bi–SiC solders.[37, 38] Electrodeposition has been already shown to improve reliability of microelectronic devices in 3D Through Silicon Via interconnection packaging.[39, 40] Recently, Sharma *et al.* developed CeO_2 nanoparticle reinforced Sn–Ag alloy by pulse co-electrodeposition technique and found a great enhancement in strength, microstructure, and successfully manipulated the residual stress to mitigate of dangerous tin whiskers.[41]

3. Pulse co- electrodeposition of Sn based composites

Initially, the pulse electrodeposition was used for decorative and jewellery applications to improve the surface appearance and shine, wear and friction, fretting corrosion resistance.[42] Recently, more attention has been paid to incorporate different nanoparticles to obtain much improved properties. There are various processing parameters in electrodeposition that affect the particle incorporation in composite deposits, such as (1) particle type, size, and shape; (2) bath pH, constituents, additives, and aging; (3) deposition variables, such as particle concentration in bath, current density, agitation, pulsing methods, and temperature.[42–44]

Composite system	Methodology	Improved properties	Reference
Sn-reinforced with CNT	Electrodeposition	Improved shear properties	[37]
Sn-Pb reinforced with Cu and TiO ₂ nanoparticles	Blending and solidification	Improved microhardness	[47]
Sn-Cu reinforced with Al ₂ O ₃ nanoparticles	Powder Metallurgy	Improved mechanical performance	[21]
Sn-Cu reinforced with Si ₃ N ₄	Powder Metallurgy	Improved wetting	[48]
Sn-Bi reinforced with SiC nanoparticles	Electro Deposition	Improved shear properties	[38]
Sn-Bi reinforced with Yttrium oxide nanoparticles	Powder Metallurgy	Improved shear strength	[33]
Sn-Ag reinforced with ZrO ₂ nanoparticles	Casting and solidification	Improved mechanical performance	[22]
Sn-Ag reinforced with SnO ₂ nanoparticles	Powder Metallurgy	Improved mechanical performance	[25]
Sn-Ag reinforced with Cu ₆ Sn ₅ , Ni ₃ Sn ₄ , FeSn ₂ nanoparticles	In situ methods	Creep resistant	[46]
Sn-Ag reinforced with CeO ₂ nanoparticles	Pulse electroplating	Whisker resistant	[41]
Sn-Ag-Cu reinforced with SiC nanoparticles	Mixing and solidifying	Improved mechanical performance	[22]
Sn-Ag-Cu reinforced with Multiwalled CNT	Powder Metallurgy	Improved mechanical performance	[34]
Sn-Ag-Cu reinforced with TiO ₂ nanoparticles	Melting route	Improved mechanical performance	[23]
Sn-Ag-Cu reinforced with TiB ₂ nanoparticles	Powder Metallurgy	Improved mechanical performance	[49]

Table 1. Nanocomposite solder produced by various routes

The different nanocomposite solders produced in literature are shown in Table 1. The composite approach has been developed mainly to improve the strength and reliability of solder joints. Nano-sized reinforcement particles in conventional solder matrices due to their effectiveness in improving the reliability by spreading the stress uniformly in the matrix.[19, 45, 46]

In this chapter, an effort has been made to discuss the strength related concerns by incorporating the reinforcement nanoparticles within the solder matrix using co-electrodeposition process.

3.1. The co-electrodeposition mechanisms

Guglielmi demonstrated the mechanism of codeposition for the first time in 1972. The mechanism provides a fundamental insight of codeposition theory.[50] According to this model the entrapment of particles is based on various adsorption processes. This is a mathematical formulation of the influence of particle content and current density on the particle codeposition rate into the metal matrix excluding particle characteristics and hydrodynamic conditions.

3.1.1. Guglielmi model

The first step involves the loose adsorption of the particles onto the electrode surface. This is a physical adsorption process. However, in the second step, the particles are attracted towards the electrode under electric field and causes a stronger adsorption of particles onto the electrode, as shown in Fig. 2.

Figure 2. Codeposition mechanism into a metal matrix.[50, 51]

As a result of strong adsorption, the particles are incorporated in the deposit and form a composite layer. This model is the simplest and is adopted for various composite systems, however, it does not account for hydrodynamic effects, particle size, type and shape in detail.

3.1.2. Celis model

Guglielmi model triggered the development of other codeposition theories by Celis, and his co-workers. They predicted the co-deposited particles content in the matrix. According to the Celis model the inert particles approach towards the cathode in a specific sequence: (1) the adsorption of ionic cloud surrounding the particle surface, (2) the force of convection currents in electrolyte also supports the particles incorporation partly, (3) the diffusion kinetics of particles across the electric double layer, (4) the adsorption of the inert particles and the absorption of ionic cloud onto the cathode, and (5) the decrease in adsorbed ionic content and their embedment in the metal coating (Fig. 3).

Figure 3. Electric double layer around the ceramic particle showing the ionic concentration and generated potential difference as a function of the distance from the charged particle suspended in electrolyte.[51]

There are various other codeposition models such as for non-Brownian motion of particles in the bath.[52, 53] Although the various developed codeposition models are important tools in the nanocomposite fabrication yet, these models are not perfect for the understanding the influences of process parameters on the codeposition rate in the metal matrix without any experimental data.

4. Factors affecting composite co-electroplating

4.1. Deposition current density

The deposition rate in electrodeposition process plays a vital role in the fabrication of nanocomposites. The number density of particles approaching the cathode surface depends on the applied electric potential, and the thickness of the growing metal is determined by the deposition current density. The rate determining step in the co-electrodeposition is when the

strong adsorption of particles on the cathode surface occurs. A strong adsorption of particles is always difficult and is improved by applying current or feeding the corresponding overpotential in the electrolyte. As a consequence, the particle incorporation in the coating increases continuously. However, at a sufficiently high current density, the codeposition rate of the coating decreases drastically. This may be caused by the limited supply of the metal ions toward cathode leading to the decrease in the particle amount.[54] The embedded particle density as a function of current density has been studied for different particle concentrations in the bath in Ref. [55]. It has been reported that at lower current densities (0.5 A dm^{-2}), the embedded particle density is poor due to a weaker adsorption of nanoparticles on the cathode. In few reports, there is a negligible effect of current density on the particle density in the matrix. [42, 56] In other cases, various optimum particle concentrations have been detected in the current density versus particle concentration graph.[51, 57–59] It is also noteworthy point that the current density not only influences the codeposition rate, but the particles present in the electrolyte also modify the current density and hence the morphology of the deposits.[60, 61]

4.2. Zeta potential

The zeta potential is a parameter used to measure surface charge of the particle in the solution, and it indicates the stability of the colloidal suspensions. A higher zeta potential means a lower degree of particle agglomeration in the electrolyte.[62] From electrodeposition point of view, the stability of the nanoparticles is an important factor for a better embedded particle density in the matrix. It has been found that for the nickel matrix composites, when the electrostatic repulsion within the dispersed particles increases, particle agglomeration decreases, and the embedded particle density increases uniformly in the nickel matrix.[62] Uniform dispersion of nanoparticles shows higher attraction toward cathode and thus produces strong adsorption. [63] The zeta potential depends on the various factors, i.e., size of particles (nano or micro), addition of surfactants, electrolyte composition, the particle shape, the bath pH, and the energy of hydration.[64–66] Bund and Thiemig reported that negatively charged particles are highly attracted when there is an excess plus charge on the electrical double layer. This observation works for various composite systems. However, in case of electrophoresis, the negatively charged particles have been successfully deposited into the nickel matrix.[68] This might be correlated to not only the zeta potential but the absolute value of the zeta potential too in addition.

4.3. Bath temperature and pH

Generally, effect of temperature is always to increase the metal grain growth rate. There are different results of the effect of temperature on various codeposition systems. For example, the nickel matrix composite reinforced with Al_2O_3 shows no increment of the volume fraction of particles with temperature.[60, 69] On the contrary, the Ni–Co alloy matrix composite shows a significant increment in the reinforced TiO_2 as a function of temperature up to 45°C . [70] Similar behavior was shown by the nickel matrix composite reinforced with SiC at 50°C . [71] Several reports are also available that show a linear decrease in the mass fraction of copper matrix composites as described in Ref. [42].

The bath pH is directly related to the surface charge density of the nanoparticles in the electrolyte. The surface charge density is generally related to the parameter termed as zeta potential. Zeta potential is a measure of the colloidal stability. The nickel matrix reinforced with the Al_2O_3 shows no effect on incorporation rate when bath pH > 2. When the bath pH is increased beyond 2, the incorporation rate declines.[60] This result is consistent with those of Verelst and his co-workers.[69] Similarly, Wang et al. observed that nickel matrix reinforced with SiC nanoparticles shows an improvement in particles incorporation rate beyond a bath pH of 5.[72] Park and his co-workers also investigated the effect of pH on nickel matrix composites reinforced with SiO_2 and TiO_2 nanoparticles. They found that the dispersion of SiO_2 is better at alkaline pH (~ 8) values rather than in acidic pH values. Moreover, for the dispersion of TiO_2 , the acidic pH (~3.5) provided better results.[73] The particle content in the composite also behaved in the similar way. They correlated this to the fact that SiO_2 has a negative zeta potential from pH 2–11. It is not clear if these effects are accompanied by a decrease of particle content below pH 2, because the SiC content of the deposits is not investigated. However, in the case of Ni– TiO_2 , the TiO_2 particles experience a point of zero charge around pH < 5 in the plating bath and particle content increases.

4.4. Bath agitation

Electrolyte agitation is always required to avoid the settling of the particles in electrolyte and to improve their movement toward the cathode. Vaezi and his co-workers observed that increasing the stirring rate up to 120 rpm increases the amount of SiC nanoparticles in the matrix but falls at a higher stirring rate. At a higher stirring rate, the flow is turbulent and not only the metal ions but the SiC particles are washed away on the cathode surface quickly.[74] A similar trend was observed by Bagheri *et al.*[75] in the electrodeposition of Ni– TiO_2 nanocomposite. Sen. *et al.*[76] also studied the effect of stirring rate on the microstructure of Ni– CeO_2 nanocomposite and found that fraction of CeO_2 particles increases up to stirring rate of 450 rpm, whereas at higher stirring rates the incorporation of CeO_2 decreases. The coelectrodeposition of ultrafine WC into Ni matrix on a rotating disk electrode with various rotation velocities in the range of 200–1200 rpm under pulse and direct current (DC) conditions is performed in Ref. [77]. This study also verified the fact that the increase in rotation speed has a beneficial effect up to a certain limit. In some studies, the ultrasound waves have been utilized in an attempt to avoid the formation of agglomerated nanoparticles in the plating bath due to the generation of large pressure causing breakdown of agglomerates. Kuo *et al.*[63] reported that the diameter of the agglomerated alumina particles may be refined by ultrasound energy, but the result of particle incorporation is not reasonable.

4.5. Particle concentration and size

Generally, the smaller particles possess higher van der Waals force of attraction or repulsion. It has been reported that the volume fraction of nanoparticles in nickel matrix increases with increasing particle concentration in the electrolyte.[60] The dependence of particle content in the deposit and consequently on the microstructure and surface properties has been studied by many authors.[78–80] In all studies, the volume fraction of the incorporated particles in the coatings with increase in the particle concentration in the plating bath up to an optimum value

and decreases again. The particle shape affects the adsorption of the particles on the cathode by varying the charge on the particle surface and the suspension stability. Regarding the effect of particle size on codeposition, different results have been reported. Such as for Ni-Co/SiC[80], an increase in the fraction of embedded particles was reported for micron-sized SiC compared to nano-SiC, while a negligible influence of particle size is observed for Ni-Al₂O₃ composite.[69] It can be explained as when two particles come closer, agglomeration occurs as the force of attraction exceeds the force of repulsion between them. The magnitude of the net forces thus produced depends on the bath parameters and the processing conditions of the system.[41]

4.6. Bath types and surfactants

The type of plating baths also affects the co-electrodeposition process. For example, few studies have been conducted on non-aqueous plating baths and organic solvents. In some cases, water has been used partially or completely mixed with organics to avoid hydrogen embrittlement and to obtain a wider processing window.[82] Shrestha *et al.* studied the codeposition of nickel matrix composite using ethyl alcohol base in nickel bath and succeeded to achieve maximum amount of particle incorporation in the Ni matrix. They also found superior wear properties of the composite coatings prepared from ethanol electrolyte compared to those obtained from Watts's type plating bath.[83] Singh *et al.* also investigated the electrodeposition of Ni-TiC composite in acetate bath using *n*-methyl formamide as non-aqueous solvent and found better composite properties.[78]

Surfactants also enhance the rate of particle incorporation in composite electrodeposition. The choice of a given surfactant depends on their charge or polarity. Cationic surfactants are widely used for increasing the particle incorporation rate in the metal matrix. They impart positive charge to the particle surface and prevent the agglomeration in the plating bath.[84] It has been observed that the cationic adsorption is more effective if the particle size is in the nanoscale.[85] According to one report, cationic surfactants can increase the particle content up to 5 times for nickel matrix composites.[57] In another study, the content can be SiC content increased up to 50 volume percent with a fluorocarbon surfactant.[42] Similar study shows that azo-cationic surfactant improved the incorporation rate up to 62.4 volume percent.[86] However, it is always recommended to use surfactants in a minute concentration in the plating bath to avoid carbon compounds in the coating.

4.7. Plating mode

Various electrodeposition modes utilizing pulsing waveforms like pulsed current (PC), pulsed reverse current, and DC have been used to improve the embedded particles density into composite matrix.[87] The application of PC technique in nickel electroplating has been shown to improve mechanical properties, wear and friction, and more uniform distribution of the particles compared to DC technique.[77]

At a given average current density, a decrease in t_{on} time induces a fine crystallite size and increases nucleation rate have been reported.[88] In addition, a longer t_{off} promotes the grain growth and the arrival of more particles near the cathode. Therefore, pulse plating is impor-

tant for co-electrodeposition of nanocomposites. For example, in Ni-SiC deposition, the application of PC results in the production of composite coatings with higher fraction of particles, and better properties than obtained with DC plating.[89] In another technique of pulse reversing, the pulsed-reverse current (PRC) technique, a stripping time is also applied to the pulse waveform, during which the surface projections are dissolved and produce more smooth deposit.[90] The Zn matrix nanocomposite reinforced with the TiO_2 nanoparticles using the PRC technique has been shown to improve the embedded TiO_2 particle density in the matrix.[91]

5. Properties of electro-composites

The original driving force for the preparation of nanocomposite solders was to improve the mechanical, thermal, and corrosion resistance of the solder alloys to utilize them in high temperature, harsh service conditions. The properties that are improved compared to the conventional Pb-Sn solder are summarized as follows:

5.1. Density

The density of a microelectronic device is very important for developing portable electronic goods. There are various reports which show a reduction in density values in nanoparticle reinforced composites. [18, 21, 41] Zhong *et al.* reported that the Al_2O_3 reinforced Sn matrix composite is lighter compared to monolithic matrix, while Babaghorbani *et al.* found that SnO_2 reinforced Sn-3.5Ag matrix did not show any change in density. This may be due to the fact that the matrix and reinforcement have the similar values of density.[21, 25]

5.2. Electrical conductivity

The electrical conductivity of a metal matrix is a function of various factors like fraction of secondary reinforcement phase, fraction of pores, size and shape, and the metal matrix. [92, 93] Nai *et al.* observed that the dispersion of CNT in the Sn based matrix does not decrease the conductivity of the matrix.[94] They correlated this fact with the low volume fraction of pores as well as reinforcement in the solder matrix. This type of behavior has been also observed by Sharma *et al.* for Sn-CeO₂ and Sn-Ag/CeO₂ nanocomposites.[41, 95] Babaghorbani *et al.* studied the electrical properties of nanocomposite solders in detail and reported that nano-sized reinforcements is advantageous in not degrading the electrical conductivity of the device, while micron sized particles can degrade the conductivity values .[96] This further confirms the unique properties of nanocomposite solders for electromigration property microelectronic packaging devices. Recently, it has been demonstrated the nanoparticles reinforced solders can be promising candidates for preventing electromigration failure in electronic packaging devices.[97]

5.3. Melting point

There is wide distribution of results on the thermal behavior of solders.[18, 22, 23, 41, 95, 98, 99] The melting points of the nanocomposite solders generally decreases with an increase in

the fraction of the nanoparticles in the matrix. Liu *et al.* reported that Sn–Ag–Cu/nano-SiC showed a reduction in melting point compared to monolithic Sn–Ag–Cu alloy. They correlated this observation to the increase in the interface surface instabilities after the addition of SiC nanoparticles. Similarly Kumar *et al.* also observed a slight depression in the melting point in CNT reinforced solder matrix. However, Nai *et al.* did not observe any significant drop in the melting point.[98, 99] Shen *et al.* while working on ZrO₂ reinforced solder the reinforcement particles, i.e., ZrO₂ nanoparticles behave as a nucleating agents and promote the nucleation of the matrix during solidification. Therefore, more nucleating sites results in grain refinement and a drop in melting point could be noticed. [22] Recently, Sharma *et al.* have found a decreased melting point of Sn–CeO₂ and Sn–Ag/CeO₂ nanocomposites and explained this behavior to the refinement of matrix grains after addition of nanoparticles.[41, 95]

5.4. Solderability

During soldering, in order to form a proper metallurgical bond between two materials, wetting must take place. There is an increase in solder wetting onto the metallic substrates after addition of the nanoparticles in the solder matrix. The high surface energy nanoparticles decrease the surface tension and wetting angle and results in the improved solderability. However, too much addition of nanoparticles in the solder may degrade the wetting properties due to the increase in agglomeration of nanoparticles in the molten alloy.[35] Additions of metallic additives also have been shown the similar behavior where the wetting decreases due to the increase in surface tension and oxidation of the reinforcing phase.[100] Recently, Sharma *et al.* investigated the solderability of Sn–Ag–Cu alloy reinforced with La₂O₃ nanoparticles in terms of spreading ratio and wetting balance measurements. They also found that the wetting is improved up to an optimum amount of La₂O₃ nanoparticles and decreases beyond that due to the increase in surface tension and melt viscosity.[19]

5.5. Microhardness

The nanocomposite solders developed have better microhardness as required for the electronics packaging industry. It has been reported that the addition of ceramic oxides or inert nanoparticles [19, 21–23, 34–37, 41, 95] can improve the mechanical performance, tensile strength, elongation and creep properties of nanocomposite solders. Moreover, the additions of nanoparticles refine the grains of the matrix as well as are adsorbed on the intermetallic to refine them. In general, there is an enhancement at the cost of ductility of the solder which is undesirable. Recently, Sharma *et al.* have produced Sn–Ag–Cu/La₂O₃ solder with an improved tensile strength as well as ductility. They explained this due to the mechanism of slip mode transition of dislocation when interacting with the La₂O₃ nanoparticles in the solder matrix.[19]

5.6. Wear and friction behavior

In various microelectronic devices and assemblies, Sn based connectors such as press fit plugs and sockets, separable interconnects in consumer electronic appliances are gaining popularity

nowadays. Gold and silver based contacts provide optimum wear resistance in sliding contacts but they are not economical. Therefore, the sliding wear and tear are important for Sn based solders may limit their applications. [101] Tin based contacts are generally susceptible to fretting wear which is a prime concern in automobile applications.[102, 103] Sn based connectors are very ductile and more sensitive to fretting wear. Hammam *et al.* investigated the wear and frictional properties of various Sn coating prepared hot dipping, electroplating, and reflow processes. They suggested that the different processing routes for Sn deposition produce different thickness of the Sn coatings and hence the intermetallic compounds on a metallic substrates. [104] In case of nanocomposite solders, Jun *et al.* reported that tin bronze reinforced with carbon fibers improves the resistance against the fretting wear appreciably.[105] Sharma *et al.* have recently found a significant enhancement on the wear resistance of Sn and Sn–Ag matrices reinforced with CeO₂ nanoparticles.[41, 95]

5.7. Electrochemical corrosion

Electrochemical behavior of Sn based coatings is important in microelectronic packaging devices. The corrosion of Sn base coatings may deteriorate the microstructural properties of the solder joints and ultimately lead to entire failure of the device. For example, in marine applications, the chlorides ions from the sea can dissolve the solder joints by forming soluble compounds.[106] There are various forms of corrosion such as pitting, crevice, and/or galvanic corrosion of solder and substrate material. Therefore the corrosion of electronic devices may impose a serious threat among microelectronics community to produce corrosion resistant solder materials. However, there is a scarcity of information of electrochemical corrosion of the solder joints.[107, 108] It has been shown that presence of Bi in Sn–Bi solder can increase the dissolution of Sn slightly in sulfuric acid solution and vigorously in nitric acid solution compared to that of pure tin.[108, 109]. It has been noticed that lead-free solders are highly corrosion resistant towards chloride ion attack compared to conventional Sn–Pb solder. [110] Recently, Sharma *et al.* proposed that use of nanoparticles is better idea to avoid the localized dissolution of Sn coatings. If the nanoparticles are added in an optimum concentration in the solder matrix, the corrosion resistance of the solder matrix can improve significantly by setting up of homogeneous corrosion instead of preferential and sudden damage. The high surface energy nanoparticles in the solder matrix reduce the corrosion potential, corrosion current, and diffusion capacitance, thus increasing passivity of the solder coating.[111]

5.8. Whisker growth mitigation

Tin whisker growth in the Sn based coatings is a serious issue in microelectronic packaging devices. The driving force of these whisker growth is the generation of compressive stresses in the coatings on storage for a long time. When plated on a metallic substrate like copper, the Cu–Sn interdiffusion across the interface may give rise to the formation of Cu₆Sn₅, Cu₃Sn etc., IMCs and grow with time causing a volume expansion of the interface. The expansion of the interface causes the setup of compressive stress in the coatings. Recently, it has been identified by various researchers that addition of nanoparticles may suppress the growth of IMCs and restrict the formation of whiskers in the matrix. Generally, the ceramic nanoparticles are very

smaller compared to size of IMCs. Therefore they can easily attach with the growing IMC in the molten metal and restrict the growth of IMCs during solidification as predicted by the surface adsorption theory.[18, 19, 22, 41]

6. Summary

Addition of nanoparticles in the solder matrix improves the microstructural properties due to the refinement in the grain size as well as the thickness of the IMC (Cu_6Sn_5 , Ag_3Sn) in the solder matrix. Wettability is improved due to the decrease in interfacial energy in presence of high surface energy nanoparticles. The higher hardness of nanosolder composites as compared to monolithic alloys can be attributed not only to the grain size and dispersion strengthening effect, but also to the refinement of the IMCs such as Cu_6Sn_5 , Ag_3Sn by ceramic nanoparticles. The melting point of the solders is minimum from an optimum reinforcement amount in the matrix, which indicates its possibility to use without any change in the existing soldering procedures. There is a rise in the resistivity of the composite matrix compared to the monolithic materials. However, the resistivity of the composites falls within the usable limits as reported for other Sn and Sn–Ag-based composites, used for electrical contact applications. The nanoscale reinforcements are added in minute concentrations and do not degrade the resistivity much if their distribution is uniform and electromigration phenomena in the composite solders. The addition of reinforcement in the Sn matrix also improves the wear resistance, which ultimately increases the coating life for application. The wear resistance of the composite coatings is better than that of the monolithic materials, and it is associated with an enhancement in the microhardness of the composite. It is also observed that composite solders possess the better corrosion resistance as compared to monolithic ones. The presence of fine Ag_3Sn compounds in composite increases the passivation of the matrix which acts as a noble barrier in addition to ceramic reinforcements against corrosion propagation. It is also observed that an incorporation of CeO_2 nanoparticles in the composite matrix reduces the compressive stresses developed in the coatings. The residual stresses of monolithic materials are negative, i.e., compressive in nature. A decline in residual stress indicates that the driving force for whisker growth can be minimized by choosing an optimum concentration of ceria, and thus, the coating life can be improved.

Author details

Ashutosh Sharma^{1*}, Siddhartha Das² and Karabi Das²

*Address all correspondence to: stannum.ashu@gmail.com

1 Department of Materials Science and Engineering, University of Seoul, South Korea

2 Department of Metallurgical and Materials Engineering, Indian Institute of Technology, Kharagpur, India

References

- [1] Tummala, R.R.. Fundamentals of Microsystems Packaging. McGraw-Hill; 2000. p. 185–210.
- [2] Alam, M.O. Study of Interfacial Reactions in Ball Grid Array (BGA) Solder Joints for Advanced Integrated Circuits (IC) Packaging, PhD Thesis, City University of Hong Kong; 2004.
- [3] Puttlitz, K.J.; Gaylon, G.T. Impact of RoHS Directive on High Performance Electronic Systems. *Journal of Materials Science: Materials in Electronics*. 2007; 18: 347–365.
- [4] Subramanian, K.N. Lead Free Electronic Solders. A Special Issue of the *Journal of Materials Science: Materials in Electronics*. New York: Springer Science; 2007. p. 55–76.
- [5] Suganuma, K. Lead Free Soldering in Electronics – Science, Technology and Environmental Impact. New York: Marcell Dekker, Inc.; 2004.
- [6] Puttlitz, K.J.; Stalter, K.A. Handbook of Solder Technology for Microelectronic Assemblies. New York: Marcell Dekker, Inc.; 2004. p. 51–55.
- [7] Abtew, M.; Selvaduray, G. Lead Free Solders in Microelectronics. *Materials Science and Engineering R*. 2000; 27: 95–141.
- [8] Guo, F. Composite Lead-Free Electronic Solders, Lead free electronics solders, A Special Issue of the *Journal of Materials Science: Materials in Electronics*. 2006; 129–145.
- [9] Alam, M.E.; Nai, S.M.L.; Gupta, M. Development of High Strength Sn–Cu Solder Using Copper Particles at Nanolength Scale. *Journal of Alloys and Compounds*. 2009; 476: 199–206.
- [10] Lai, L.H.; Duh, J.G. Lead-Free Sn–Ag and Sn–Ag–Bi Solder Powders Prepared by Mechanical Alloying. *Journal of Electronic Materials*. 2003; 32: 215–220.
- [11] El-Daly, A.A.; Hammad, A.E. Elastic Properties and Thermal Behavior of Sn–Zn Based Lead-Free Solder Alloys. *Journal of Alloys and Compounds*. 2010; 505: 793–800.
- [12] Miao, H.-W.; Duh, J. Microstructure Evolution in Sn–Bi and Sn–Bi–Cu Solder Joints Under Thermal Aging. *Materials Chemistry and Physics*. 2001; 71: 255–271.
- [13] Nogita, K.; Nishimura, T. Nickel-Stabilized Hexagonal (Cu, Ni)₆Sn₅ in Sn–Cu–Ni Lead-Free Solder Alloys. *Scripta Materialia*. 2008; 59: 191–194.
- [14] Lin, K.L.; Shih, P.C. IMC Formation on BGA Package With Sn–Ag–Cu and Sn–Ag–Cu–Ni–Ge Solder Balls. *Journal of Alloys and Compounds*. 2008; 452: 291–297.

- [15] [15]Wu, C.M.L.; Yu, D.Q.; Law, C.M.T.; Wang, L. Properties of Lead-Free Solder Alloys With Rare Earth Element Additions. *Materials Science and Engineering R*. 2004; 44: 1–44.
- [16] Suganuma, K. Advances in Lead-Free Electronics Soldering. *Current Opinion in Solid State and Materials Science*. 2001; 5: 55–64.
- [17] Coombs, C.F. *Printed Circuits Handbook*. USA: McGraw Hill; 2001. p. 45.1–45.9.
- [18] Shen, J.; Chan, Y.C. Research Advances in Nano-Composite Solders, *Microelectronics Reliability*. 2009; 49: 223–234.
- [19] Sharma, A.; Baek, B.G.; Jung, J.P. Influence of La_2O_3 Nanoparticle Additions on Microstructure, Wetting, and Tensile Characteristics of Sn–Ag–Cu Alloy. *Materials and Design*. 2015; 87: 370–379.
- [20] Jin, S.; McCormack, M. Dispersoid Additions to a Pb-Free Solder for Suppression of Microstructural Coarsening. *Journal of Electronic Materials*. 1994; 23: 735–739.
- [21] Zhong, X.L.; Gupta, M. Development of Lead-Free Sn–0.7Cu/ Al_2O_3 Nanocomposite Solders With Superior Strength. *Journal of Physics D: Applied Physics*. 2008; 41: 095403.
- [22] Shen, J.; Liu, Y.C.; Han, Y.J.; Tian, Y.M.; Gao, H.X. Strengthening Effects of ZrO_2 Nanoparticles on the Microstructure and Microhardness of Sn–3.5Ag Lead-Free Solder. *Journal of Electronic Materials*. 2006; 35: 1672–1679.
- [23] Liu, P.; Yao, P.; Liu, J. Effect of SiC Nanoparticle Additions on Microstructure and Microhardness of Sn–Ag–Cu Solder Alloy. *Journal of Electronic Materials*. 2008; 37(6): 874–879.
- [24] Tsao, L.C.; Chang, S.Y. Effects of Nano- TiO_2 Additions on Thermal Analysis, Microstructure and Tensile Properties of Sn3.5Ag0.25Cu solder. *Materials and Design*. 2010; 31: 990–993.
- [25] Sivasubhramaniam, V.; Bosco, N.S.; Janczak-Rusch, J.; Cugnoni, J.; Botsis, J. Interfacial Intermetallic Growth and Strength of Composite Lead Free Solder Alloy Through Isothermal Aging. *Journal of Electronic Materials*. 2008; 37: 1598–1604.
- [26] Babaghorbani, P.; Nai, S.M.L.; Gupta, M. Development of Lead-Free Sn–3.5Ag/ SnO_2 Nanocomposite Solders. *Journal of Materials Science: Materials in Electronics*. 2009; 20: 571–576.
- [27] Miller, C.M.; Anderson, I.E.; Smith, J.F. A Viable Tin Lead Solder Substitute: Sn–Ag–Cu. *Journal of Electronic Materials*. 1994; 23: 595–601.
- [28] Aggarwal, A.O.; Abothu, I.R.; Raj, P.M.; Sacks, M.D.; Tummala, R.R. Lead-Free Solder Films Via Novel Solution Synthesis Routes. *IEEE Transactions on Components and Packaging Technologies*. 2007; 30: 486–493.

- [29] Conway, P.P.; Fu, E.K.Y.; Williams, K. Precision High Temperature Lead-Free Solder Interconnections by Means of High-Energy Droplet Deposition Techniques. *CIRP Annals – Manufacturing Technology*. 2002; 51: 177–180.
- [30] Hsiao, L.-Y.; Duh, J.-G. Synthesis and Characterization of Lead Free Solders With Sn–3.5Ag– x Cu ($x=0.2, 0.5, 1.0$) Alloy Nanoparticles by the Chemical Reduction Method. *Journal of Electrochemical Society*. 2005; 159(9): J102–J109.
- [31] Hsiung, C. K.; Chang, C. A.; Tzeng, Z. H.; Ho, C. S.; Chien, F. L. Study on Sn–2.3Ag Electroplated Solder Bump Properties Fabricated by Different Plating and Reflow Conditions. 9th Electronics Packaging Technology Conference. 2007; pp. 719–724.
- [32] Ruythooren, W.; Attenborough, K.; Beerten, S.; Merken, P.; Fransaer, J.; Beyne, E.; Hoof, C.V.; Boeck, J.D.; Celis, J.P. Electrodeposition for the Synthesis of Microsystems. 200; 10: 101–107.
- [33] Wang, X.; Liu, Y.C.; Wei, C.; Gao, H.X.; Jiang, P.; Yu, L.M. Strengthening Mechanism of SiC-Particulate Reinforced Sn–3.7Ag–0.9Zn Lead-Free Solder. *Journal of Alloys and Compounds*. 2009; 662–665.
- [34] Fouzder, T.; Gain, A.K.; Chan, Y.C.; Sharif, A.; Yung, W.K.C. Effect of Nano Al_2O_3 Additions on the Microstructure, Hardness and Shear Strength of Eutectic Sn–9Zn Solder on Au/Ni Metallized Cu Pads. *Microelectronics Reliability*. 2010; 50: 2051–2058.
- [35] Liu, X.; Huang, M.; Wu, C.M.L.; Wang, L. Effect of Y_2O_3 particles on microstructure formation and shear properties of Sn–58Bi solder. *Journal of Materials Science: Materials in Electronics*. 2010; 21: 1046–1054.
- [36] Nai, S.M.L.; Wei, J.; Gupta, M. Lead-Free Solder Reinforced with Multiwalled Carbon Nanotubes, *Journal of Electronic materials*. 2006; 35(7): 1518–1522.
- [37] Nai, S.M.L.; Wei, J.; Gupta, M. Influence of Ceramic Reinforcements on the Wettability and Mechanical Properties of Novel Lead-Free Solder Composites. *Thin Solid Films*. 2006; 504: 401–404.
- [38] Chen, Z.; Shi, Y.; Xia, Z.; Yan, Y. Properties of Lead-Free Solder SnAgCu Containing Minute Amounts of Rare Earth, *Journal of Electronic materials*. 2003; 32(4): 235–243.
- [39] Choi, E.K.; Lee, K.Y.; Oh, T.S. Fabrication of Multiwalled Carbon Nanotubes-Reinforced Sn Nanocomposites for Lead-Free Solder by an Electrodeposition Process. *Journal of Physics and Chemistry of Solids*. 2008; 69: 1403–1406.
- [40] Shin, Y.S.; Lee, S.; Yoo, S.; Lee, C.W. Mechanical and Microstructural Properties of SiC-Mixed Sn–Bi Composite Solder Bumps by Electroplating. *Proceedings of Electronics Packaging Technology Conference*. 2009; 1–4.

- [41] Jung, D.H.; Sharma, A.; Kim, K.H.; Choo, Y.C.; Jung, J.P. Effect of Current Density and Plating Time on Cu Electroplating in TSV and Low Alpha Solder Bumping. *JMPEG*. 2015; 24: 1107–1115.
- [42] Roh, M.H.; Sharma, A.; Lee, J.H.; Jung, J.P. Extrusion Suppression of TSV Filling Metal by Cu–W Electroplating for Three-Dimensional Microelectronic Packaging. *Metallurgical and Materials Transactions A*. 2015; 46: 2051–2062.
- [43] Sharma, A.; Bhattacharya, S.; Das, S.; Das, K. Fabrication of Sn–Ag/CeO₂ Electro-Composite Solder by Pulse Electrodeposition. *Metallurgical and Materials Transactions A*. 2013; 44: 5587–5601.
- [44] Hovestad, A.; Janessen, L.J.J. Electrochemical Co-Deposition of Inert Particles in a Metallic Matrix. *Reviews in Applied Electrochemistry*. 1995; 40: 519–527.
- [45] Kedward, E.C.; Wright, K.W.; Tennett, A.A.B. The Development of Electrodeposited Composites for Use as Wear Control Coatings on Aero Engines. *Tribology*. 1974; 7(5): 221–227.
- [46] Stankovic, V.D.; Gojo, M. Electrodeposited Composite Coatings of Copper With Inert, Semiconductive and Conductive Particles. *Surface and Coatings Technology*. 1996; 81: 225–232.
- [47] Liu, J.P.; Guo, F.; Yan, Y.F.; Wang, W.B.; Shi, Y.W. Development of Creep-Resistant, Nanosized Ag Particle-Reinforced Sn–Pb Composite Solders. *Journal of Electronic Materials*. 2004; 33(9): 958–963.
- [48] Choi, S.; Lee, J.G.; Guo, F.; Bieler, T.R.; Subramanian, K.N.; Lucas, J.P. Creep Properties of Sn–Ag Solder Joints Containing Intermetallic Particles. *JOM*. 2001; 53: 22–26.
- [49] Lin, D.C.; Liu, S.; Guo, T.M.; Wang, G.X.; Srivatsan, T.S.; Petraroli, M. An Investigation of Nanoparticles Addition on Solidification Kinetics and Microstructure Development of Tin–Lead Solder. *Materials Science and Engineering A*. 2003; 360: 285–292.
- [50] Mohd Salleh, M.A.A.; Mustafa Al Bakri, A.M.; Kamarudin, H.; Bnhussain, M.; Zan@Hazizi, M.H.; Flora, S. International Conference on Physics Science and Technology (ICPST 2011). In: *Physics Procedia*. 2011; 22: 299–304.
- [51] Wei, J.; Nai, S.M.L.; Wong, C.K. Gupta, M. Enhancing the Performance of Sn–Ag–Cu Solder with the Addition of Titanium Diboride Particulates. *SIMTech technical reports*. 6(1), pp. 29–32.
- [52] Guglielmi, N. Kinetics of Deposition of Inert Particles From Electrolytic baths, *Journal of Electrochemical Society*. 1972; 119(8): 1009–1012.
- [53] Celis, J.P.; Roos, J.R., Buelens, C. A Mathematical Model for the Electrolytic Codeposition of Particles With a Metallic Matrix. *Journal of Electrochemical Society*. 1987; 134(6): 1402–1408.

- [54] Fransaer, J.; Celis, J.P.; Roos J.R. Analysis of the Electrolytic Codeposition of Non-Brownian Particles With Metals. *Journal of Electrochemical Society*. 1992; 139(2): 413–425.
- [55] Vereecken, P.M.; Shao, I.; Searson, P.C. Particle Codeposition in Nanocomposite Films. *Journal of Electrochemical Society*. 2000; 147(7):2572–2575.
- [56] Guo, D.; Zhang, M.; Jin Z.; Kang R. Effects of Chloride Ion on the Texture of Copper and Cu-ZrB₂ Coatings Electrodeposited from Copper Nitrate Solution in Different Plating Modes. *Journal of Materials Science and Technology*. 2006; 22: 643–646.
- [57] Gay, P.A.; Bercot, P.; Pagetti, J. (2001). Electrodeposition and characterisation of Ag-ZrO₂ electroplated coatings. *Surface and Coatings Technology*. 2001; 140: 147–154.
- [58] Graydon, J.W.; Kirk, D.W. Suspension Electrodeposition of Phosphorus and Copper, *Journal of Electrochemical Society*. 1990; 137: 2061–2066.
- [59] Chang, Y.S.; Lee, J.Y. Wear Resistant Nickel Composite Coating from Bright Nickel Baths with Suspended Very Low Concentration Alumina. *Materials Chemistry and Physics*. 1988; 20: 309–321.
- [60] Celis, J.P.; Roos, J.R. Kinetics of the Deposition of Alumina Particles from Copper Sulfate Plating Baths. *Journal of Electrochemical Society*. 1977; 124: 1508–1511.
- [61] Rudnik, E. Influence of Surface Properties of Ceramic Particles on Their Incorporation into Cobalt Electroless Deposits. *Applied Surface Science*. 2008; 225: 2613–2618.
- [62] Sautter, F.K. Electrodeposition of Dispersion-Hardened Nickel-Al₂O₃ Alloys. *Journal of Electrochemical Society*. 1963; 110: 557–560.
- [63] Watson, S.W. Electrochemical Study of SiC Particle Occlusion during Nickel Electrodeposition. *Journal of Electrochemical Society*. 1993; 140: 2235–2238.
- [64] Simunkova, H.; Pessenda-Garcia, P.; Wosik, J.; Angerer, P.; Kronberger, H.; Nauer G.E. The Fundamentals of Nano- and Submicro-scaled Ceramic Particles Incorporation into Electrodeposited Nickel Layers: Zeta Potential Measurements. *Surface and Coatings Technology*. 2009; 203: 1806–1814.
- [65] Kuo, S.-L.; Chen, Y.-C.; Ger, M.-D.; Hwu, W.-H. Nano-particles Dispersion Effect on Ni/Al₂O₃ Composite Coatings. *Materials Chemistry and Physics*. 2004; 86: 5–10.
- [66] Morterra, C.; Cerrato, G.; Ferroni, L. Surface Characterization of Yttria-stabilized Tetragonal ZrO₂ Part 1. Structural, Morphological, and Surface Hydration Features. *Materials Chemistry and Physics*. 1994; 37: 243–257.
- [67] Wernet, J.; Feke, D.L. Effects of Solids Loading and Dispersion Schedule on the State of Aqueous Alumina/Zirconia Dispersions. *Journal of the American Ceramic Society*. 1994; 77: 2693–2698.

- [68] Kim, S.K.; Yoo H.J. Formation of Bilayer Ni–SiC Composite Coatings by Electrodeposition. *Surface and Coatings Technology*. 1998; 108–109: 564–569.
- [69] Bund, A.; Thiemi D. Influence of Bath Composition and pH on the Electrocodeposition of Alumina Nanoparticles and Nickel. *Surface and Coatings Technology*. 2007; 201: 7092–7099.
- [70] Low, C.T.J.; Willis, R.G.A.; Walsh, F.C. Electrodeposition of Composite Coatings Containing Nanoparticles in a Metal Deposit. *Surface and Coatings Technology*. 2006; 201: 371–383.
- [71] Verelst, M.; Bonino, J.P.; Rousset, A. Electroforming of Metal Matrix Composite: Dispersoid Grain Size Dependence of Thermostructural and Mechanical Properties. *Materials Science and Engineering A*. 1991; 135: 51–57.
- [72] Abed, F.A. Deposition of Ni–CO/TiO₂ Nanocomposite Coating by Electroplating. *International Journal of Advanced research*. 2015; 3: 241–246.
- [73] Hamal, K.; Gyawali, G.; Rajbhandari (Nyachhyon), A.; Lee, S.W. Effect of Bath Temperature on Electrochemical Codeposition of Nickel Silicon Carbide Composite. *International Journal of Chemistry and Pharmaceutical Sciences*. 2014; 2: 777–782.
- [74] Wang, S.C.; Wei, W.C.J. Kinetics of Electroplating Process of Nano-sized Ceramic Particle/Ni Composite. *Materials Chemistry and Physics*. 2003; 78: 574–580.
- [75] So-Yeon, P.; Myung-Won, J.; Jae-Ho, L. Nano Oxide-Dispersed Nickel Composite Plating. *Electronic Materials Letters*. 2013; 9: 801–804.
- [76] Vaezi, M.R.; Sadrnezhaad, S.K.; Nikzad, L. Electrodeposition of Ni–SiC Nano-composite Coatings and Evaluation of Wear and Corrosion Resistance and Electroplating Characteristics. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2008; 315: 176–182.
- [77] Bagheri, P.; Farzam, M.; Mousavi, A.B.; Hosseini, M. Ni–TiO₂ Nanocomposite Coating with High Resistance to Corrosion and Wear. *Surface and Coatings Technology*. 2010; 204: 3804–3810.
- [78] Sen, R. Synthesis and Characterization of Pulse Electrodeposited Ni–CeO₂ Nanocomposite Coatings. PhD Thesis. IIT Kharagpur; 2011.
- [79] Stroumbouli, M.; Gyftou, P.; Pavlatou, E.A.; Spyrellis, N. Codeposition of Ultrafine WC Particles in Ni Matrix Composite Electrocoatings. *Surface and Coatings Technology*. 2005; 195: 325–332.
- [80] Singh, D.K.; Singh, V.B. Electrodeposition and Characterization of Ni–TiC Composite Using *N*-Methylformamide Bath. *Materials Science and Engineering A*. 2012; 532: 493–499.

- [81] Ramesh Bapu, G.N.K.; Jayakrishnan, S. Development and Characterization of Electro Deposited Nickel–Titanium Carbo Nitride (TiCN) Metal Matrix Nanocomposite Deposits. *Surface and Coatings Technology*. 2012; 206: 2330–2336.
- [82] Shrestha, N.K.; Takebe, T.; Saji, T. Effect of particle size on the co-deposition of diamond with nickel in presence of a redox-active surfactant and mechanical property of the coatings. *Diamond and Related Materials*. 2006; 15:1570–1575.
- [83] Bakhit, B; Akbari, A. Effect of Particle Size and Co-deposition Technique on Hardness and Corrosion Properties of Ni–Co/SiC Composite Coatings. *Surface and Coatings Technology*. 2012; 206: 4964–4975.
- [84] Gores, H. J.; Barthel, J. M. G. Nonaqueous Electrolyte Solutions: New Materials for Devices and Processes Based on Recent Applied Research. *Pure and Applied Chemistry*. 1995; 67: 919–930.
- [85] Shrestha, N.K.; Saji, T. Non-aqueous Composite Plating of Ni-ceramic Particles Using Ethanol Bath and Anti-wear Performance of the Coatings. *Surface and Coatings Technology*. 186 (2004) 444.
- [86] Pompei, E.; Magagnina, L.; Lecis, N.; Cavallotti, P.L. Electrodeposition of Nickel–BN Composite Coatings. *Electrochimica Acta*. 2009; 54: 2571–2574.
- [87] Ewa, R.; Lidia, B.; Łukasz, D.; Maciej, M. Electrodeposition of Nickel/SiC Composites in the Presence of Cetyltrimethylammonium Bromide. *Applied Surface Science*. 2010; 256: 7414–7420.
- [88] Shrestha, N.K.; Kobayashi, G.; Saji, T. Electrodeposition of Hydrophobic Nickel Composite Containing Surface-Modified SiO₂ Particles under the Influence of a Surfactant with an Azobenzene Moiety. *Chemistry Letters*. 2004; 33(8): 984–985.
- [89] Jung, A.; Natter, H.; Hempelmann, R.; Lach E. Nanocrystalline Alumina Dispersed in Nanocrystalline Nickel: Enhanced Mechanical Properties. *Journal of Materials Science*. 2009; 44: 2725–2735.
- [90] Bicelli, L.P.; Bozzini, B.; Mele, C.; D'Urzo, L. A Review of Nanostructural Aspects of Metal Electrodeposition. *International Journal of Electrochemical Science*. 2008; 3: 356–408.
- [91] Gyftou, P.; Pavlatou, E.A. & Spyrellis N. Effect of Pulse Electrodeposition Parameters on the Properties of Ni/nano–SiC Composites. *Applied Surface Science* 2008; 254: 5910–5916.
- [92] Chandrasekar, M.S.; Pushpavanam, M. Pulse and Pulse Reverse Plating—Conceptual, Advantages and Applications. *Electrochimica Acta*. 2008; 53: 3313–3322.
- [93] Fustes, J.; Gomes, A.; da Silva Pereira, M.I. Electrodeposition of Zn–TiO₂ Nanocomposite Films—Effect of Bath Composition. *Journal of Solid State Electrochemistry*. 2008; 12: 1435–1443.

- [94] Chang, S.Y.; Chen, C.F.; Lin, S.J.; Kattamis, T.Z. Electrical Resistivity of Metal Matrix Composites. *Acta Materialia*. 2003; 51: 6191–6302.
- [95] Weber, L.; Dorn, J.; Mortensen, A. On the Electrical Conductivity of Metal Matrix Composites Containing High Volume Fractions of Non-Conducting Inclusions. *Acta Materialia*. 2003; 51: 3199–3211.
- [96] Nai, S.M.L.; Wei, J.; Gupta, M. Effect of Carbon Nanotubes on the Shear Strength and Electrical Resistivity of a Lead-Free Solder. *Journal of Electronic Materials*. 2008; 37(4): 515–522.
- [97] Sharma, A.; Bhattacharya, S.; Das, S.; Fecht, H.-J.; Das, K. Development of Lead Free Pulse Electrodeposited Tin Based Composite Solder Coating Reinforced with *Ex Situ* cerium Oxide Nanoparticles. *Journal of Alloys and Compounds*. 2013; 574: 609–616.
- [98] Babaghorbani, P.; Nai, S.M.L.; Gupta, M. Reinforcements at Nanometer Length Scale and the Electrical Resistivity of Lead-Free Solders. *Journal of Alloys and Compounds*. 2009; 478: 458–461.
- [99] Sharma, A.; Xu, D.E.; Chow,.; Mayer, M.; Sohn, H.-R.; Jung, J.P. Electromigration of Composite Sn–Ag–Cu Solder Bumps. *Electronic Materials Letters*. In press, DOI: 10.1007/s13391-015-4454-x.
- [100] Kumar, K.M.; Kripesh, V.; Tay, A.A.O. Influence of Single-Wall Carbon Nanotube Addition on the Microstructural and Tensile Properties of Sn–Pb Solder Alloy. *Journal of Alloys and Compounds*. 2008; 455: 148–158.
- [101] Nai, S.M.L.; Wei, J.; Gupta, M. Improving the Performance of Lead-Free Solder Reinforced With Multi-Walled Carbon Nanotubes. *Materials Science and Engineering A*. 2006; 423: 166–169.
- [102] Lee, H.Y.; Sharma, A.; Kee, S.H.; Lee, Y.W.; Moon, J.T.; Jung, J.P. Effect of Aluminium Additions on Wettability and Intermetallic Compound (IMC) Growth of Lead Free Sn (2 wt. % Ag, 5 wt. % Bi) Soldered Joints. *Electronic Materials Letters*. 2014; 10:997–1004.
- [103] Baumann, W.; Degner, W.; Fiedler, J.; Horn, J.; Richter, G.; Weissmantel, C. A Study of Frictional, Wear and Contact Resistance Performance of Tin Alloy Coatings. *Thin Solid Films*. 1983; 105: 305–318.
- [104] Wu, J.; Pecht, M. Fretting Corrosion Studies for Lead Free Alloy Plated Contacts. *Electronics Packaging Technology Conference*. 2002; pp. 20–24.
- [105] Sankara Narayanan, T.S.N.; Park, Y.W.; Lee, K.Y. Fretting-Corrosion Mapping of Tin-Plated Copper Alloy Contacts. *Wear*. 2007; 262: 228–233.
- [106] Hammam, T. The Impact of Sliding Motion and Current Load on the Deterioration of Tin-Coated Connectors. *Proceedings of the Fourty Fifth IEEE Holm conference on Electrical contacts*. 1999; pp. 203–212.

- [107] Jun, Z.; Jincheng, X.; Wei, H.; Long, X.; Xiaoyan, D.; Sen, W.; Peng, T.; Xiaoming, M.; Jing, Y.; Chao, J.; Lei, L. Wear Performance of the Lead Free Tin Bronze Matrix Composite Reinforced by Short Carbon Fibers. *Applied Surface Science*. 2009; 255: 6647–6651.
- [108] Song, F.; Lee, S.W.R. Corrosion of Sn–Ag–Cu Lead-free Solders and the Corresponding Effects on Board Level Solder Joint Reliability. *Proceedings of 56th Electronic Components and Technology Conference*. 2006; pp. 891–898.
- [109] Rosalbino, F.; Angelini, E.; Zanicchi, G.; Carlini, R.; Marazza, R. Electrochemical Corrosion Study of Sn–3Ag–3Cu Solder Alloy in NaCl Solution. *Electrochimica Acta*. 2009; 54: 7231–7235.
- [110] Mohanty, U.S.; Lin, K.L. Electrochemical Corrosion Study of Sn–XAg–0.5Cu Alloys in 3.5% NaCl Solution. *Journal of Materials Research*. 2007; 22: 2573–2581.
- [111] Wu, B.Y.; Chan, Y.C.; Alam, M.O.; Jillek, W. Electrochemical Corrosion Study of Pb-Free Solders. *Journal of Materials Research*. 2006; 21: 62–70.
- [112] Li, D.; Conway, P.P.; Liu, C. Corrosion Characterization of Tin–Lead and Lead Free Solders in 3.5 wt.% NaCl Solution. *Corrosion Science*. 2008; 50: 995–1004.
- [113] Sharma, A.; Das, S.; Das, K. Electrochemical corrosion behavior of CeO₂ nanoparticle reinforced Sn–Ag based lead free nanocomposite solders in 3.5 wt.% NaCl bath. *Surface and Coatings Technology*. 2015; 261:235–243.