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Surface Morphology Study of Nanostructured Lead-Free Solder Alloy Sn-Ag-Cu Developed by Electrodeposition: Effect of Current Density Investigation

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Abstract - Nanostructured lead-free solder Sn-Ag-Cu (SAC) was developed by electrodeposition method at room temperature. Electrolite bath which comprised of the predetermined quantity of tin methane sulfonate, copper sulfate and silver sulfate were added sequentially to MSA solution. The methane sulphonic acid (MSA) based ternary Sn-Ag-Cu bath was developed by using tin methane sulfonate as a source of Sn ions while the Cu+ and Ag+ ions were obtained from their respective sulfate salts. The rate of the electrodeposition was controlled by variation of current density. The addition of the buffer, comprising of sodium and ammonium acetate helped in raising the pH solution. During the experimental procedure, the pH of solution, composition of the electrolite bath, and the electrodeposition time were kept constant. The electrodeposited rate, deposit composition and microstructure were investigated as the effect of current density. The electrodeposited solder alloy was characterized for their morphology using Field Emission Scanning Electron Microscope (FESEM). In conclusion, vary of current density will play significant role in the surface morphology of nanostructured lead-free solder SAC developed.

Key words - Nanostructured; electrodeposition, lead-free solder, alloy

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Introduction

Worldwide legislation for the removal or reduction of lead and other hazardous material has prompted a large number of lead-free solder developments. The lead-free solder, mostly tin-rich is the alternative solder over the conventional solder is to restrict the use of and inclusion of lead in most materials up to a certain acceptable composition [1].

The drive for development of lead-free solder is towards system that can replicate conventional lead containing alloy behavior besides fulfill the following requirements: good wettability, low melting temperature, good mechanical properties, good resistance to mechanical and thermal fatigue, corrosion resistance, good electrical properties, health and environment friendly, easy availability and low material cost[2].

Regardless of the great finding from the lead-free solder related research, it was found that the main disadvantages of the lead-free solder is high melting temperature [3], [4], [5], insufficient fatigue resistance and low reliability characteristic inhibit wide practical application in industry [6]. The increase of melting temperature in lead-free solder has already been a disadvantages to the manufactures since it leading to significant capital expenditure and resulting in the increase of product cost [7].

Nanostructured materials exhibit a variety of properties that are different and often considerably improved in comparison with those of conventional coarse-grained materials due to the super fine grain sizes and consequent high density of interfaces. These include increased strength/hardness, enhanced diffusivity, improved ductility/ toughness, reduced density, reduced elastic modulus, higher electrical resistivity, increased specific heat, higher coefficient of thermal expansion, lower thermal conductivity, and superior soft magnetic properties[8-14].

Thus, development of nano-composite and nanostructured solder is introduced to enhance the creep and thermo-mechanical fatigue resistance of solder materials by the strengthening effect of the reinforcement. Appropriately fine and homogeneously distributed particles throughout the solidified solder joint help in producing good strengthening effect. The probability of crack initiation can be reduced and the fatigue resistance can be enhanced. The reduction of the structural grain size of nanostructured materials are seen as the best solution to increase the creep and thermo-mechanical fatigue resistance of solder materials [7]. In this paper, the effect of current density on the structural grain size will be investigated using FESEM analysis.

Materials and Methods

Experimental Materials and Chemicals

Sn-Ag-Cu bath will be developed uses tin methane sulfonate acid (local manufacture product, 50 wt. % in H2O), silver sulfate (Sigma Aldrich, 99%) and copper sulfate (Sigma Aldrich, 99%). Source of Sn ions will be obtained from the methane sulphonic acid (MSA) based ternary while the Cu^+ and Ag^+ ions will be obtained from their respective sulfate salts. Bath with combinations of $Sn^{2+,}$ Cu^+ and Ag^+ ions will be formulated based on the SAC 305 as the basis. Sodium and ammonium acetate (Merck, Ph Eur) act as buffer help in raising the pH of the bath.

Preparation of substract

The electrodeposition of Sn-3.0Ag-0.5Cu solder alloy will be done using chronopotentiometry (galvanostatic) method of the potentiostat-galvanostat. Before deposition, the substrates will be thoroughly clean with soap water, rinsed, dried and degrease using trichloroethylene. Throughout the electrodeposition, the tin substract will be set as the anode and the copper substract will be set as the working electrode, cathode. Nickel coated (5μm thick) copper substrates will be used as cathode since the Ni film underneath solder help in masking positively charged ions (cations) signal emanating from the electron-providing (negative) cathode clad substrate during EDS analysis. This Ni film was electrodeposited using a commercial Ni plating bath at 55°C at current density of 40mAcm^{-1} for 7 min to obtain about 5 μm thick film.

Preparation of electrolite bath

Tin methane sulfonate acid will act as a source of Sn ions while the Cu^+ and Ag^+ ions will be obtained from their respective sulfate salts. Predetermined quantity of tin methane sulfonate acid, copper sulfate and silver sulfate were added sequentially at room temperature in beaker, while being stirred with magnetic stirrer. This will be followed by the addition of sodium or ammonium acetate act as buffer help in raising the pH of the bath. The composition of electrolyte bath and experimental condition are listed in Table 1.

Electrodeposition of SAC alloy

The cell was set up with the tin substract will be set as the anode and the nickel coated copper substract as the working electrode, cathode. A deposition area of 1cm^2 will be defined by masking the copper substrate using adhesive tapes. All the depositions will be carried out at room temperature for duration of 1h at a current density between 1mAcm^{-1} and 20mAcm^{-1}. After deposition the films will be rinsed in water, dried and characterized for microstructure and element analysis. The electrodeposited solder alloy was characterized for their morphology using Field Emission Scanning Electron Microscope (FESEM).

Table 1: The bath composition and electrodeposition conditions of Sn–Ag-Cu alloys

No	Chemical	Values/Unit	
1	Tin methane sulfonate acid	0.813	M
2	Silver sulfate	0.0556	M
3	Copper sulfate	0.007874	M
4	Thiourea	0.2	M
5	pH	2	pH
6	Current density	1~25	mAcm^{-2}
7	temperature	25	˚C

Results and Discussions

Figures 1-5 show FESEM micrographs of the surface morphology of the electrodeposited SnAgCu films from electrodeposition on copper substrate at various current densities ranging from 1 to 20 mA/cm^2 and the deposition process lasted 60 min. It is possible to observe that, even with the same composition, the deposits have different morphologies under different controlled parameter[15]. A variety of morphological patterns for the electrodeposits obtained with different direct current is obtained[16]. With increasing current densities (e.g., 5–10 mA/cm2), smooth, uniform and compact electrodeposits are obtained, while at higher current densities (e.g., 15– 20 mA/cm^2) the deposits are porous.

Figure 1a exhibits the deposited film at current density of 1 mA/cm^2, where the deposits are smooth but less uniform and fine grains were observed with the grains size range below than 100nm and sphere in shape. In comparison, as evidenced from Fig. 1b and c, as the current density was increased at 5 and 10 mA/cm^2, the deposited film exhibits compact and fine grain indicating that the increase of current density results in significant improvement in surface morphology and much finer grains. However, at higher current densities (e.g., 15– 20 mA/cm^2, as in figure 1d and 1e), the roughness and porosity of the deposits increased. Larger grained structure was obtained leading to a rougher surface with cracks or crevices[16].

Nevertheless, alloy deposition becomes mass transfer limited or very close to the mass transfer limit at very high current densities. Extreme current densities can be attributed to the very high overpotential, which causes the metal ions from solution to move rapidly towards cathode. This may lead to a depletion of the metal ion concentration of the aqueous solution adjacent to the cathode and the electrode surface gets polarized.

A greater change in potential is required to maintain the current so as to overcome the concentration polarization and consequently, the system enforces hydrogen ions to be discharged at a very high rate. As the current density increases further, the hydrogen evolution competes with the metal deposition. The hydrogen gas evolutions give rise to bubble formation that often gets incorporated in the crystal lattice. The phenomena resulting in porous and spongy deposits develops when current density exceeds a critical value[16], [17].

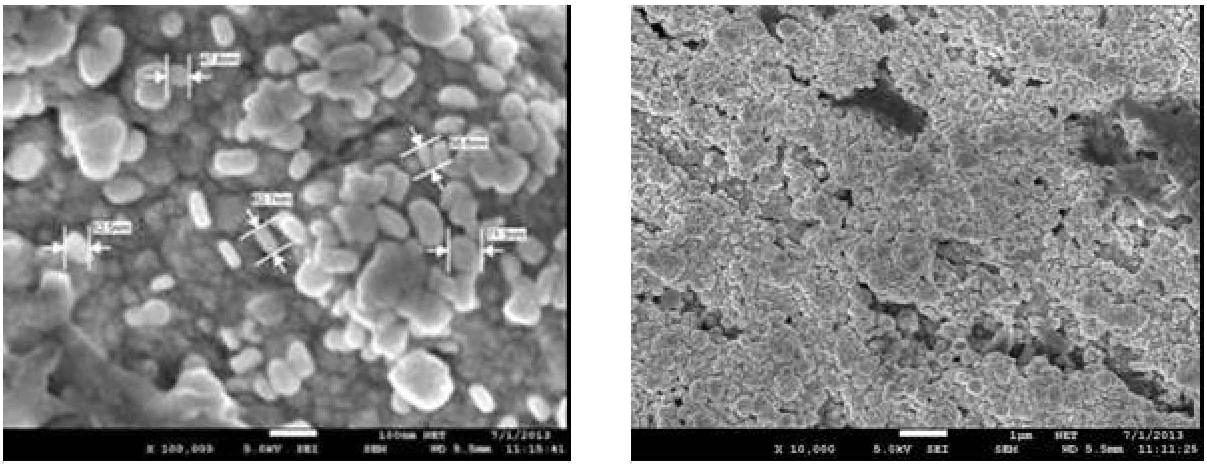

Figure 1: FESEM micrographs of the surface morphology of the electrodeposited SAC films at current density of 1mA/cm^2 (left: 10 000 x magnification, and right: 100 000 x magnification)

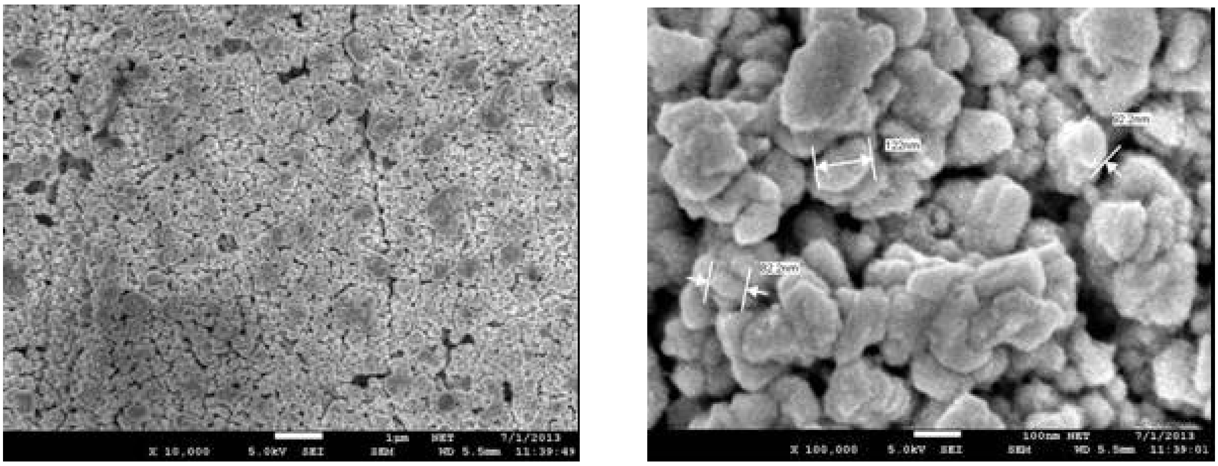

Figure 2: FESEM micrographs of the surface morphology of the electrodeposited SAC films at current density of 5mA/cm^2 (left: 10 000 x magnification; and right: 100 000 x magnification)

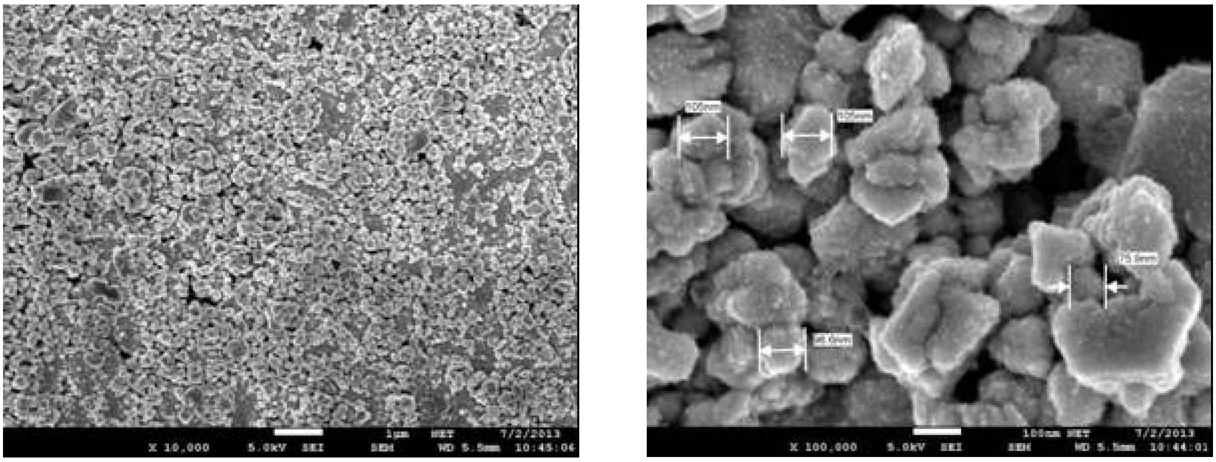

Figure 3: FESEM micrographs of the surface morphology of the electrodeposited SAC films at current density of 10mA/cm^2 (left: 10 000 x magnification; and right: 100 000 x magnification)

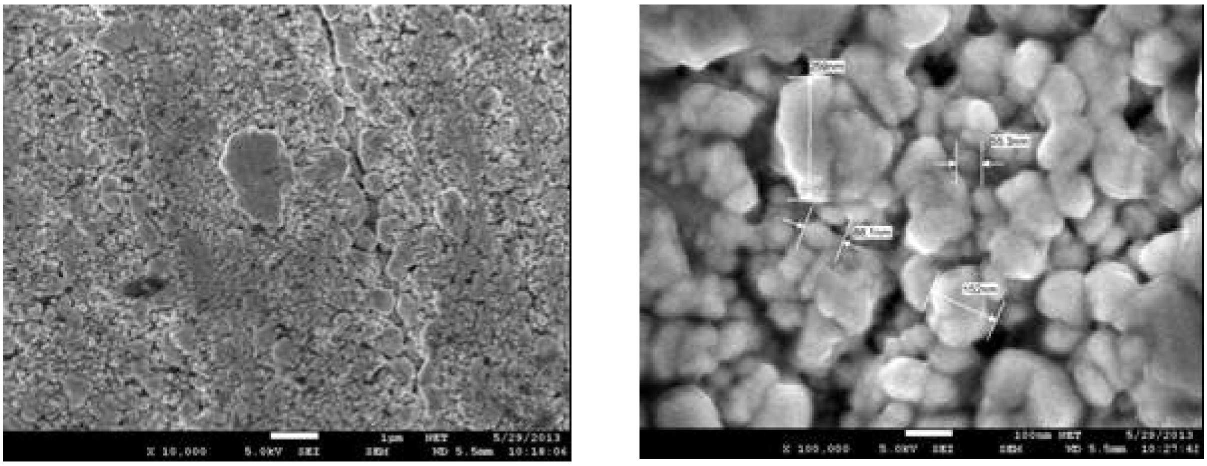

Figure 4: FESEM micrographs of the surface morphology of the electrodeposited SAC films from electrodeposition on copper substrate at current density of 15mA/cm^2 (left: 10 000 x magnification; and right: 100 000 x magnification)

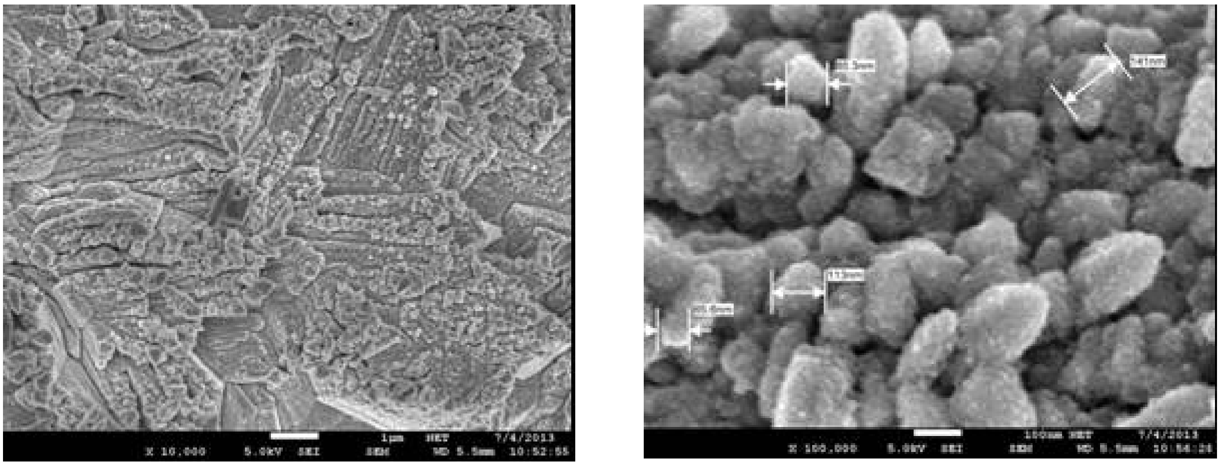

Figure 5: FESEM micrographs of the surface morphology of the electrodeposited SAC films current density of 20mA/cm^2 (left : 10 000 x magnification, and right: 100 000 x magnification)

Conclusions

A relation between current density and surface morphology has been obtained for the electrodeposited Sn-Ag-Cu alloy. It is possible to observe that, even with the same composition, the deposits have different morphologies under different current density. At low current density of 1 mA/cm^2, the deposits are smooth but less uniform and fine grains were observed with the grains size range below than 100nm and sphere in shape. Increasing current densities (e.g., 5– 10 mA/cm2) resulting in smooth, uniform and compact electrodeposits. The fine grain deposited film indicating that the increase of current density results in significant improvement in surface morphology. The grains size range was increased more than 100nm. Contradictorily, higher current densities (e.g., 15– 20 mA/cm^2), the grains size range has achieved more than 200nm leading to a rougher surface and increase the porosity of the deposits.

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