Geometrical effects of Cu@Ag core-shell nanoparticles treated flux on the growth behaviour of intermetallics in Sn/Cu solder joints

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Abstract Solder ball of initial diameter 1.4 mm, was reflow soldered with Cu substrate at 523.15 K using flux doped with Cu@Ag core-shell nanoparticles (NPs) in the proportion 0 - 2 wt. %. The solders were then air cooled to room temperature. The use of NPs, by reducing the base height (H) of the solder and enhanced the diameter (W) of the solder, caused an overall increase in the spread ratio of the solder. The altered magnitudes of heat and mass transfer in these geometrically different but constant volume specimens were analyzed using finite element method. The occurrence of differential concentration gradient, radial thermal gradient and velocity magnitudes, in solders with differing geometry were numerically elaborated. The Cu₆Sn₅ intermetallic compound (IMC) formed at the Cu/Sn interface, was obtained to be the thickest for the specimen using undoped flux, whereas it was found to be smallest for the sample processed with flux containing 0.5 % NPs. From the growth kinetics

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study, it has been inferred that IMC thickness is linearly proportional to the geometrical parameter H and W^b , with $b < 1$.

Keywords Electronic Materials · Intermetallic compounds · Crystal Growth · Thermogravimetric Analysis · Diffusion · Finite Element Method

1 Introduction

In context of electronic packaging technology, emerging trends and environmental regulations have created new challenges on both the manufacturing and reliability of electronic devices. Nowadays, the demands for higher functionality and performance has led the manufacturing industries to design and fabricate downsized and miniaturized electronic devices. The electronic packaging sectors are showing tendency to shift from 2D integrated circuits (ICs) to 3D ICs technology [1] and the diameter of solder bumps is going to become as small as nearly $10\ \mu\text{m}$ in future (μ -bumps) [2]. Soldering is a common procedure for forming interconnections. During the preparation of Pb-free solder joints, the formation of intermetallics compound (IMC) via interfacial reaction is a necessity to ensure that a complete joint is formed. However, the brittleness of the Cu_6Sn_5 imposes a significant challenge to the overall reliability of the solder joints and a control in its thickness remains a major topic of current research trend.

With the development of miniaturized electronic equipment, the volume fraction of IMC for solder joint has increased with the downsized of solder bumps. Therefore, many research works have been carried out to study the size effect on IMC growth behavior to build the relation between the solder joint size and the morphology of IMC grains. Thus, dissolution rate of the Cu into liquid solder during reflow, overall Cu pad consumption, average IMC layer thickness and Cu_6Sn_5 grain size, have been assessed with respect to the size of the solder ball adjacent to the Cu substrate [3,4,5]. The size effect in these previous research works was, about the influence of different volumes of solder ball on the IMC growth behavior. In essence, the size effect (especially induced by transport mechanisms such as diffusion and advection of IMC forming species), can occur due to geometrical factors for a given solder volume as well. For an example, when the solder ball of a given diameter spreads differentially on Cu substrate owing to varied wetting properties, the diffusion length and influx of Cu from substrate changes owing to the variation of relative heights and interfacial area. Therefore, an experiment about soldering with same volume of solder ball and different wetting property (different height and width of solder bulk after spreading) can provide a design methodology to investigate the relation between the geometrical parameter and the IMC growth.

Studies have shown that wettability of solder can be improved by adding Ag nanoparticles in flux for soldering [6]. The use of metallic nanoparticles to alter the geometrical structure of solder bulk and design the interfacial microstruc-

ture of solder-substrate interface, can open a new paradigm in microelectronic packaging sector.

In order to reduce the excessive influence of Ag element on IMC growth behavior and considering the high cost of silver, Cu@Ag core-shell nanoparticles have been chosen as the nanostructures to dope the flux. For this research, Cu@Ag core-shell nanoparticles have been synthesized in accordance to the methodology described in our previous article [7]. These nanoparticles were doped into the flux at different weight proportions to prepare composite flux; and then composite flux was applied over Cu substrate, before performing soldering reflow experiments with Sn/Cu system. The geometrical dimensions and interfacial IMCs resulting in the resultant Sn/Cu joints have been investigated. At the same time, numerical simulation is also used to model the heat and mass transfer inside the liquid solder. We try to computationally explore Cu saturation behavior, temperature distribution and the liquid solder velocity magnitudes on specimens with different spreading rate and then, further study the IMC growth behavior. This research could be useful in designing Cu₆Sn₅ crystal size and morphology, and thus be meaningful for realizing a reliable interconnection with solder joint produced in several geometrical shapes.

2 Experimental method

2.1 Materials

The Cu@Ag core-shell nanoparticles used for this study were made by chemical reduction method. The detail information about the preparation can be mentioned in the article [7]. The crystallite size and phases of the Cu@Ag nanoparticles were investigated by X-Ray diffractometer (XRD-6000). The sample was exposed to Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) with the scanning speed of 2 deg/min. The morphology of nanoparticle were characterized by the field emission scanning electron microscopy (NOVA Nano-SEM 450) equipped with energy disperse X-ray spectroscopy. Fig. 1 (a) shows the X-ray diffraction patterns for the as-prepared Cu@Ag core-shell nanoparticles for this research, which confirmed that the phase of attained particles are composed of Cu and Ag and no obvious oxide peak appeared in this XRD pattern. At the same time, from the lining analysis of EDS in inserted figure of Fig. 1 (a), the Cu core was surround well by Ag shell. The thermogravimetric analysis system (DSC822/TGA/SDTA851, Switzerland) was carried with a heating rate of 10 °C/min to investigate the thermal stability of six kinds of Cu@Ag core-shell nanoparticles, for TGA test in atmospheric condition and for DSC under nitrogen environment. From TGA and DSC analysis in Fig. 1 (b), for TGA curve below 473.15 K (200 °C), there is a slight decrease because of the weight loss of the absorbed water and decomposition of some capping agent on the surface of core-shell nanoparticles. This is corresponding to the endothermic peak at about 473.15 K (200 °C) in the DSC thermograph in Fig. 1(b). From TGA analysis in Fig. 1(b), it can be deduced that the

Fig. 1 Characterization of as-synthesized Cu@Ag core-shell nanoparticles: (A) XRD spectra and SEM figure (insert picture); (b) TGA and DSC curve.

weight gain is only 6% under air condition for whole heating process. What is more, until 523.15 K of solder temperature, the weight gain is less than 2%. Therefore, the Cu@Ag core-shell nanoparticle is thermal stable enough for soldering.

2.2 Preparation of Sn/Cu solder joints using heterogeneous flux

Materials for preparation of solder joint: Pure Sn solder ball (Dalian Golden Saddle Welding Limited Company, China; purity: 99.99%, Melting point: 505.04 K), polycrystalline Cu substrate (Qingyuan Metal Materials Limited Company, China; purity: 99.99%, Melting point: 1356.55 K), rosin flux (AMTECH: NC-559-ASM) and as-synthesised Cu@Ag core-shell nanoparticles.

The procedure of the solder joint preparation make a reference of Ref. [8]. The Cu sheet dimensions is 15 mm × 5 mm × 100 μm. Due to remove the surface oxides film of Cu sheet, it was cleaned in 5% HCl solution (vol.%) with ultrasonic vibration, then rinsed with deionized water and dried in acetone to used as substrate for soldering. For preparation of composite flux, mixed nanoparticles and rosin flux (AMTECH: NC-559-ASM) in a flask together, the Cu@Ag core-shell nanoparticles at weight proportion of 0 wt.%, 0.2 wt.%, 0.5 wt.%, 1 wt.% and 2 wt.% of flux, and, then subjected to stirring as well as ultra-sonication for 30 min. The composite flux containing NPs was applied over the Cu substrate. Ceramics chips using as the matrix to fix the volume of applied flux. After the application of flux, Sn solder ball of initial diameter ($\phi = 1400 \mu\text{m}$), were placed over the Cu substrate and the system was subjected to isothermal reflow at 523.15 K within reflow oven (Forced Convection, FT02) for durations of t (10 - 120 s). After the reflow soldering process, the samples were subjected to air cooling with the experimental time-temperature relationship shown by Fig. 2.

Fig. 3 shows the schematic sketch of initially spherical solder ball before spreading and the final state after spreading. To evaluate the wetting propriety, as Fig. 3, different contact angle (θ) and final central height (H), spread diameter (W), and spread ratios, were measured for solders with 0 wt.%, 1 wt.% and 2 wt.% NPs doped in flux, separately. Due to the same volume of

Fig. 2 Cooling curve for solders placed in air media after isothermal reflow. In the figure, $t = 0$ represents the end point of the soldering reflow and start of air cooling.

Fig. 3 Schematic sketch for geometrical value about contact angle and spread ratio.

solder ball and spread ratio different, the result can infer that the presence of nanoparticles in flux alter the geometrical value of $\frac{2H}{W}$ by changing the value of H , w , $S_{spread-ratio}$ and contact angle θ .

3 Mathematical formulation

3.1 Transient Cu concentration distribution in liquid solder for isothermal stage

Three-dimensional geometries and mesh (with tetrahedral mesh elements) are constructed within Salome 7.8.0 preprocessing software [9]. The transient evolution of concentration (C) in mol/cm³ of Cu species within the molten Sn solder at a given time t , is described by the following partial differential equation (PDE):

$$\frac{\partial C}{\partial t} = \nabla \cdot D_{Cu} \nabla C - (\vec{u} \cdot \nabla) C \quad (1)$$

At 523.15 K, the diffusion coefficient (D_{Cu}) of Cu in molten Sn solder is approximately equal to 6.44×10^{-9} m²/s [10,11]. The second term in right hand side of Eq. 1 consisting of $\vec{u}$, that characterizes the advection of Cu, is computed from incompressible Navier-Stokes equation (as detailed in section 3.2). The initial condition for C in the solder domain is taken as 0. In the planar boundary at the bottom of the solder, adjacent to the initial solder-substrate interface with area of magnitude (A_{spread}); dirichlet condition (BC) of 1.59×10^{-3} mol/cm³ is applied for the concentration variable. Zero flux BC is applied for this variable at the top curvature surface boundary adjacent to the ambient surrounding. Eq. 1, along with incompressible Navier-Stokes equation were solved for a total simulation time of 120 s using finite element method (FEM) in Elmer software [12,13]. Paraview 5.0.1 [14] is utilized as the visualization or post-processing software.

3.2 Variation of temperature and velocity in liquid solder during cooling condition

For the air cooling process from an initial reflow temperature of 523.15 K, the growth kinetics of Cu₆Sn₅ intermetallics compound is more pronounced in liquid state of the solder as compared to the after solidification stage. Thus, the range of temperatures above the melting point of solder is taken as the scope of the research. The PDE or energy equation for transient cooling heat transfer process in the computational domain of post-spread Sn solder, is described mathematically as:

$$\rho C_p \left(\frac{\partial T}{\partial t} + \vec{u} \cdot \nabla T \right) = k_{lq} \nabla^2 T \quad (2)$$

In Eq. 2, the variable T is temperature of liquid solder, whereas the material properties ρ , k_{lq} and C_p are respectively the density, thermal conductivity and specific heat capacity of the medium. The fluid flow within the liquid Sn is described by the following incompressible Navier-Stokes equation:

$$\nabla \cdot \vec{u} = 0 \quad (3)$$

$$\rho \frac{\partial \vec{u}}{\partial t} + \rho (\vec{u} \cdot \nabla) \vec{u} = \nabla \cdot [-pI + \nu (\nabla \vec{u} + (\nabla \vec{u})^T)] + \vec{F}_{vol} \quad (4)$$

where, p , ν and α are respectively the fluid pressure, dynamic viscosity and thermal expansivity of the liquid medium. The value of α for Sn solder is taken to be equal to $6.5 \times 10^{-5} \text{ K}^{-1}$ [12]. In Eq. 4, I is the unit tensor. Within the framework of incompressible N-S equation, the variation of fluid density with temperature, along the direction of gravitational force is addressed by the Boussinesq approximation. The corresponding component of total volumetric body force ($\vec{F}_{vol}$) in Eq. 4 accounting to this density variation is expressed as:

$$\vec{F}_{gz} = -\rho [1 - \alpha(T - T_o)] \vec{g} \quad (5)$$

where, $\vec{g}$ = acceleration due to gravity and T_o is the reference temperature of 298 K.

The initial temperature of the medium is set as 523.15 K and velocity is set as zero. The pressure throughout the solder liquid domain is assumed to be equal to the atmospheric pressure.

Robin boundary conditions (BCs) as given by the following equation, has been employed to describe the heat exchange with the ambient surrounding and the Cu substrate.

$$k_{lq} \frac{\partial T}{\partial n} = h_{coeff}(T - T_{film}) \quad (6)$$

where, h_{coeff} is the heat transfer coefficient with air/Cu substrate and T_{film} is the external temperature of the thin film layer at the boundary or interface. The magnitude of T_{film} can be assumed to be the average of the transient temperatures of the solder domain and the surrounding air. The value of heat transfer coefficient in context of the convection heat transfer process at solder top surface in contact with air is taken as $15 \text{ W/m}^2\text{K}$. In context of heat exchange to the Cu substrate during cooling procedure, the interfacial heat transfer coefficient is assigned to represent the coefficient, in accordance to the following formula:

$$h_{int} = \lambda t^{-n} \quad (7)$$

where, the amplitude λ equals $800 - 11500 \frac{J}{s^{1+n}m^2K}$ depending on the presence of thermal contact resistance (R_{th}), t is time and the exponential index, $n = 0.03$ [15]. The amplitude for transient heat transfer coefficient is lower at the interface of central region, owing to the presence of trapped air bubbles that can induce larger thermal contact resistance [12]. At the periphery region, characterized by lower R_{th} , λ can be higher. In context of velocity variable, no slip boundary condition is applied to the region of the interface boundary whereas zero flux BC is set at the top surface of the solder.

The set of Eqs. 2, 3, 4, along with the initial conditions and BCs for the T and $\vec{u}$ variables, are solved using ElmerSolver of Elmer software. For the numerical simulation of heat transfer and fluid flow in context of transient cooling procedure of Sn liquid, via Elmer software, the temperature dependence of ρ , k_{th} , C_p and ν [16,17,18,19,20] has been utilized in the FEM model. The method of compound energy formalism, has been utilized to compute the specific heat capacity of Sn solder in OpenCalphad software [21,22]. The

Fig. 4 Element distribution in solder processed with 2 wt.% NPs doped in flux: (a) BSE image; (b - d) Ag, Cu and Sn mapping using EPMA, respectively;

Navier-Stokes equations (3 and 4) have been solved along with mass transfer equation 1, to simulate the concentration variable of Section 3.1.

4 Results and Discussion

4.1 EPMA results for solder joint processed with NPs doped flux

Fig. 4 (a) shows microstructure of the Sn/Cu solder joint processed with 2 wt.% NPs in flux, wherein the Cu_6Sn_5 intermetallics is seen to be formed at the interface of solder and substrate. Figs. 4 (b - d) illustrates elemental distribution of Ag, Cu, and Sn, respectively. In the figures, the portions in the solder bulk, where compounds such as Ag_3Sn and Cu_6Sn_5 exist, the Ag and Cu phase are shown as dense region by EPMA whereas the Sn is shown to have lower molar proportion than it surrounding Sn rich region. This means that the core-shell nanoparticles are transported to the bulk region during reflow and subsequent cooling. Further more, from the Fig. 4 (b), some Ag rich phase slightly appeared at the interface of Sn/Cu. This implies that some Cu@Ag core-shell NPs is absorbed at the grain boundary of Cu_6Sn_5 at the beginning of soldering, and this is in line with the similar findings by [23,24,25].

4.2 Spreading kinetics of solders under inertial driving force

It can be seen from Fig. 5 that the contact angle θ and $\tan\frac{\theta}{2}$, decrease as the percentage of Cu@Ag nanoparticles in the flux increases, corresponding with the final wetting state in cross-sectional SEM micrographs. The contact angle decreases from the 49.31° for 0 wt.% NPs to 39.5° for 2 wt.% NPs doped in flux. Effectively, spread ratio and wettability of solder can be enhanced significantly with flux doped Cu@Ag core-shell nanoparticles, which can be verified from the SEM figure in Fig. 5. In the work of [6], it has been reported that Ag nanoparticles added into the flux act as surface-active agent to improve the effectiveness of the flux, sufficiently wet the solder and improve the wettability during soldering; and this present study utilizing Cu@Ag core-shell nanoparticles in the flux, shows a similar trend with their work. The plausible explanation for wetting behavior in this research is that wetting property can be enhanced by the nanoparticle which is favorable for accelerated interfacial reaction or chemical interactions between liquid solder and Cu substrate.

The use of flux at the interface of Sn/Cu is aimed at increasing the wettability by decreasing the effective contact angle [26]. The metallic nanoparticles with a very large ratio of surface area to volume, have enormous surface energy. Therefore, the wettability of the solder also improved by doping NPs in flux. Another effect of Cu@Ag nanoparticles on wettability is via the enhancement of thermal conductivity of flux film. As it has been mentioned in the work of Ref. [27] that the thermal conductivity of nanofluid is enhanced by introducing Cu nanowires. In this current study, during isothermal reflow inside furnace, the Cu substrate (with high thermal conductivity) will get heated quicker and the heat can be transferred more quickly to the solder through flux containing nanoparticles. The enhancement of heat transfer from substrate to solder due to the action of nanoparticles in flux can substantially contribute to the greater spreading of solder liquid over Cu substrate.

For sufficiently large Weber number (We), inertial forces dominate the spreading kinetics of liquid solder in solid Cu substrate. For the initially spherical solder drop of radius (R_{sphere}), the base radius (R), that spreads with time, can be written as following [28, 29]:

$$R = \left(\frac{\gamma_{sv} R_{sphere}}{\rho} \right)^{\frac{1}{4}} \times t^{\frac{1}{2}} \quad (8)$$

Assuming γ_{sv} , R_{sphere} and solder density (ρ) do not change with t, and differentiating Eq. 8, with respect to time, we get the expression for spread velocity of solder interface as:

$$v = \frac{dR}{dt} = \left(\frac{\gamma_{sv} R_{sphere}}{\rho} \right)^{\frac{1}{4}} \times \frac{t^{-\frac{1}{2}}}{2} \quad (9)$$

In Eq. 9, it can be inferred that spread velocity is greater for larger value of interfacial surface energy γ_{sv} . Now, the surface energy is related to final contact angle by the following expression:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos\theta \quad (10)$$

Fig. 5 Graphical plot to present the variation of contact angle and spread ratio for solders with designed flux + NPs.

Table 1 Final dimensions of solders after spreading at different ratio due to the alteration in the weight percentage of Cu@Ag nanoparticles in rosin flux.

Solder type	wt.% NPs in flux	$\frac{2H}{W} = \tan \frac{\theta}{2}$	Spread ratio	$\theta(^{\circ})$
I	0	0.46	0.76	49.31
II	0.5	0.37	0.81	41.62
III	2	0.29	0.85	39.52

The subscripts l,s and v in Eq. 10 denote liquid, solid and vapor phase respectively. In accordance to this equation, lowered contact angle is characterized by larger magnitude of γ_{sv} . Hence, the addition of Cu@Ag nanoparticles in the flux, as evidenced by experimental reduction in magnitude of θ (Table 1), can be thought as the cause behind enhancement of the magnitude of γ_{sv} and increment of the spread velocity of the solder on flux applied Cu substrate.

4.3 Geometrical effects on solder joints processed with doped flux

4.3.1 Cu distribution in liquid solder under isothermal condition

By inducing a differential attainment of spread ratio and final contact angle, via the usage of nanoparticles-doped flux, the geometrical contact area between the Cu substrate and liquid solder is practically varied at a constant volume. The use of larger proportion of Cu@Ag core-shell nanoparticles is characterized

Fig. 6 Transient distribution of Cu concentration in liquid solder for: (a) solder with pure flux and (b) solder with flux + 2% NPs during isothermal reflow at 523.15 K.

with the decrease in the value of contact angle and subsequent enlargement of effective interfacial area for Cu diffusion. On the other hand, the spreading at same volume requires the effective height or diffusion length of solder to reduce as the spreading is enhanced. Table 1 presents the final equilibrium dimensions for solder bumps of fixed volume and variable spread rate. For evaluation of geometric effect of solder samples on the Cu concentration in liquid solder during soldering, a finite element analysis (FEA) based simulation of Cu diffusion from the substrate through interface spread area into the solder at reflow holding temperature of 523.15 K is presented. The computational domain consists of the molten Sn solders of geometries type I, II and III of Table 1, representing the solder processed with flux respectively composed of 0, 0.5 % and 2 % Cu nanoparticles.

The results of transient numerical simulation of Cu concentration, for sample I with pure flux (Fig. 6 (a)) and sample III with flux consisting 2% NPs (Fig. 6 (b)), are shown in Fig. 6. From the figure, it can be inferred that the liquid solder III gets saturated with Cu, quite earlier than type I. By 30 s, both specimen attain their saturation state with Cu concentration limit of 1.59×10^{-3} mol/cc. Thus, it can be concluded that Cu from the substrate side, experiencing smaller diffusion length in context of the sample III with smaller contact angle or smaller $\frac{2H}{W}$ value as of Fig. 3, can reach faster to the opposite end of the sample, thereby contributing to the quicker attainment of saturation phase.

Fig. 7 shows time-based evolution data of transient Cu concentration at point P located on the top of solders and the inset figure shows the Cu concentration distribution corresponding to 4 s for samples I, II and III during isothermal reflow soldering, at 523.15 K. From the trend of the curves in picture, it can be known that the Cu concentration of the top point P for solder

Fig. 7 The graphical plots present the simulated values of transient Cu concentration at top point P of Fig. 3 for solder samples I, II and III. The inset shows the overall composition of the test solders at $t = 4$ s.

III with $\frac{2H}{W} = 0.29$, gets fully saturated with Cu comparatively faster than the solder sample I of $\frac{2H}{W} = 0.46$. Therefore, it can be deduced that the magnitude of $\frac{2H}{W}$ at equilibrium during spreading, has a significant influence on the rate of Cu saturation. As it will be discussed later, the amount of diffusion of Cu into the solder bulk during reflow subsequently controls the growth kinetics of both the primary and interfacial IMC.

Considering that the Z-axis is along the normal direction from the planar solder-substrate interface, Fig. 8 (a) shows the plot of Cu concentration gradient ($\frac{\delta C}{\delta Z}$) with time, along Z direction for sample I at lines OP, O₁P₁, O₂P₂, O₃P₃ (legends elaborated through the inset image) under soldering isothermal condition at 523.15 K. Similarly, Fig. 8 (b) also shows the time-based evolution of Cu concentration gradient ($\frac{\delta C}{\delta Z}$) for sample III. Along the Z direction, when soldering time at isothermal reflow stage is 10 s, the slope of average concentration gradient ($\frac{\delta C}{\delta Z}$) curve in Fig. 8 (b) for sample III ($\frac{2H}{W} = 0.29$) is smaller than sample I ($\frac{2H}{W} = 0.46$) of Fig. 8 (a). So, Cu concentration of sample III reaches its saturation limit earlier than the sample I. This implies that when the solder III gets saturated with Cu, there still exists diffusion driven flow of Cu in Z direction in sample I. It is now noteworthy to mention that for a given isothermal reflow duration and for a constant volume for samples I and II, the geometrical difference indicated by magnitude of $\frac{2H}{W}$, causes greater influx of Cu from substrate in sample I as compared to sample III. The geometry driven Cu transport is more dominant along central line OP as compared to the peripheral O₃P₃ for the two samples. As shown by the curves of Fig. 8 (a)

Fig. 8 Simulated values of $\frac{\Delta C}{\Delta z}$ with time for sample (a) I and (b) III, show that the concentration gradient also vary along the radial distance (R). The concentration gradient is plotted against R for the specimens I, II, and III corresponding to the time point (c) 10 s, and (d) 20 s.

and (b), the larger $\frac{2H}{W}$ value of sample I, causes Cu transport along O_3P_3 for longer duration as compared to the O_3P_3 line of sample III.

Fig. 8(c) and (d), respectively show the variation of $\frac{\delta C}{\delta Z}$ along R direction from the solder center for $t = 10$ and 20 s respectively. As shown by both images, the magnitude of concentration gradient for sample I is much larger than that of sample II and sample III. Thus, the use of Cu@Ag nanoparticles in flux, causes a significant effect on Cu diffusion rate. Comparing the two figures, it can be understood that $\frac{\delta C}{\delta Z}$, decreases with the advent of reflow duration, which means the attainment of saturation decreases the driving force for Cu diffusion in the Z direction.

Above all, from the inspect of Z direction and R direction, the driving force and rate of Cu saturation are controlled by the value of $\frac{2H}{W}$, which means the geometry of solder bulk has significant effect on the Cu concentration distribution inside the liquid solder under the isothermal soldering stage.

4.3.2 Temperature and velocity distribution in liquid solder during air cooling

For the experimental air cooling given by Fig. 2, the surrounding air temperature of the solder bulk cools from the temperature of 523.15 K at a cooling rate of 0.18 K/s. For the solder with very small Biot number ($Bi \ll 1$) the conduction heat transfer dominates over the convection heat transfer, and thus

Fig. 9 The simulation results of temperature distribution of sample A (a), sample B (b) and sample C (c) at 523.15 K for 10s.

the average bulk solder temperature decrease rate as obtained from the simulation is observed to be equivalent to that of the ambient surrounding. As shown in simulation results of Fig. 9, thermal gradient radially exist between center and periphery for sample I, sample II and sample III, and this can be explained by the composite action of (i) larger thermal diffusivity of molten solder [30], and (ii) differential thermal contact resistances of the interfaces at the center and periphery [31,32,33,34]. In general, with the improvement of wettability of solder bulk through NPs adding into flux and subsequent enlargement of interfacial area, the difference of thermal gradient will be more significant between center and periphery of solder bulk. For cooling duration, difference of thermal gradient still exist in solder bulk, which will induce large thermal diffusivity in solder. Therefore, the relatively greater interfacial heat transfer coefficient at the peripheral areas of the solder-substrate interfaces imposes heat transfer to be radially outward, so the IMC growth orientation will be influenced according to the research of [12].

Fig. 10 shows the flow velocity of liquid solder along the R direction during cooling stage when $t = 10$ s after the commencement of air cooling. Comparing the flow velocity zone for sample I, II and III, it can be observed that sample I has the highest velocity magnitude (0.019 m/s) at the center-top part (the red colored regime in the inset figure) of solder bulk. From the figure it can be observed that the lower spread area of sample I, causes its velocity magnitude to decrease at a greater rate along the radial coordinates. The sample III, although it has a lowest magnitude of velocity at the top center region, is characterized by a small decrement in velocity magnitude (outside the red colored region in the inset image), along the radially outward direction.

In summary, the geometrical spreading differences in solder using flux with different proportion of NPs, can induce differing magnitudes of radial thermal gradients and velocity magnitudes in the solder during liquid cooling, and thus can alter the morphology and size of resultant intermetallic compounds at the interface.

Fig. 10 The simulation results of liquid solder velocity for R direction of the solder geometry for samples I, II and III, at $t = 10$ s from the start of air cooling. The embedded figure shows the top view for the velocity magnitudes of the samples.

4.4 Growth kinetics of interfacial IMC

4.4.1 Morphology and thickness of film layers

In order to compare the morphology and the thickness of solder joint corresponding to flux with 0%, 0.2%, 0.5%, 1% and 2% Cu@Ag core-shell NPs doped, the cross sectional micrographs of interface are shown in Fig. 11. With the increase of reflow time duration, the Cu_6Sn_5 tend to grow as elongated prismatic whiskers in case of Sn/Cu solder joint with pure flux system. This whiskering effect is slightly reduced in case of sample treated with NPs doped flux. The spreading enhancement by nanoparticles containing flux can counteract the compressive stress generated during IMC growth, and so the whiskers are relatively suppressed. It is significant to distinguish the IMC morphology for solder reflowed within and beyond 10 s. Regardless of the flux type, the IMC for solder cooled after reflow of 10 s, is characterized by the presence of nucleated and partially developed intermetallics; whereas those cooled after 60 and 120 s of reflow have fully developed prismatic IMCs. Moreover, the nucleation density of IMC particles for solder cooled after reflow for 10 s, is more pronounced for solders with NPs containing flux. This is attributed to the heterogeneous nucleation phenomena on the localized sites of nanoparticles [35]. As elaborated by the simulation pictures of Fig. 6, the top portion of the bulk solder is yet to be saturated with Cu for $t \leq 10$ s; and thus for such lowered reflow duration, the precipitation driven prismatic IMC growth during cooling

Fig. 11 The SEM cross sectional images of the IMC morphology of sample with flux doped 0%, 0.2%, 0.5%, 1% and 2% NPs soldering for 10 s, 60 s and 120 s at 523.15 K.

Fig. 12 Variation in the thickness of IMC layers as a function of the content of NPs added into flux.

is suppressed. In case of reflow isothermal time is 60s and 120s; with the liquid solder solution saturated with Cu, the mechanism of screw dislocation driven growth of IMCs is pronounced and thus faceted planes appear at the surface of after-cooled Cu₆Sn₅ [36, 12].

4.4.2 Kinetics of interfacial reaction

The IMC growth kinetics at the interface of Sn/Cu solder joints can be modeled by the following empirical power law:

$$h = K \times t^n \quad (11)$$

where h is the thickness of the IMC layer during reflow; K is the rate constant for interfacial reaction; n is the time exponent; and t is the interfacial reaction time. When $n = 1/3$, the interfacial IMC growth follows the parabolic law and controlled by grain boundary diffusion [37]; when $n = 1/2$, the interfacial IMC growth follows the parabolic law and controlled by volume diffusion [38]; and, when $n = 1$, the interfacial IMC growth follows the linear law and controlled by interfacial reaction [39].

With natural logarithm on both sides of Equation 11, it can be rewritten as given below:

$$\log h = \log K + n \log t \quad (12)$$

Fig. 12 (a) and (b) shows the average thickness of IMC as function of reflow time for the samples processed with flux constituting several proportions of Cu@Ag nanoparticles. As shown by the figure, the interfacial IMC thickened parabolically, which means that the growth mechanism of IMC growth is governed by the diffusion controlled growth theory. Moreover, as shown in Fig. 12 (b), $\log h$ has a linear relationship with $\log t$, which can be utilized via linear fitting method, to deduce the value of “ n ”. For all types of samples, the value of n , was obtained within the range of 0.23-0.27, thereby indicating that the interfacial IMC growth during isothermal soldering was controlled by grain boundary diffusion of Cu atoms.

In general, the thickness of Cu_6Sn_5 compound increases with an increase in reflow duration. It is interesting to note that the thickness of IMC is the largest for solder using undoped flux. At $t = 120$ s, the thickness of IMC for solder processed with undoped flux is $3.7 \mu\text{m}$. As this sample has the largest “ H ” value, the solder height after initial spreading is very dominant for the IMC growth kinetics during precipitation. The samples with flux containing 1 % and 2 % NPs in flux, have the intermediate thickness, owing to their larger “ $W = 2R$ ” values, that influence the ripening kinetics during isothermal reflow. The solders with flux containing 0.2 % and 0.5 % NPs in flux, have the lowest IMC thickness, as their “ H ” and “ W ” both are in the intermediate ranges. At reflow duration of 120 s, the IMC thickness for solder joint prepared with flux constituting 0.5 % Cu@Ag nanoparticles, is around $2.89 \mu\text{m}$. From this we can infer that, the IMC growth kinetics depends on “ H^a ” and “ W^b ” of the solders after spreading. Here, we can broadly say that $a \approx 1$ and $b < 1$. Future works must be aimed at finding the mathematical relationship associating growth kinetics with these geometrical parameters.

5 Conclusions

The following conclusions can be drawn from this study:

1. Sn/ Cu joints were prepared using reflow soldering 523.15 K and then subjected to air cooling. The flux that has to be applied over Cu substrate at the start of reflow soldering was doped with Cu@Ag core-shell nanoparticles (NPs) in the proportion from 0 - 2 wt. %.
2. Cu@Ag core-shell nanoparticles doped flux enhanced the spreading of Sn solder at the constant volume, by reducing central height (H) and increasing effective width (W). The spreading ratio increased from the 0.76 without Cu@Ag core-shell nanoparticles to 0.85 with 2 wt.% Cu@Ag core-shell nanoparticles doped in flux. At the same time, the geometrical parameter value $\frac{2H}{W}$ decreased from 0.46 for pure flux to 0.29 for flux + 0.2 wt. % NPs.
3. The thickness of interfacial Cu₆Sn₅ IMC for solder processed with undoped flux at reflow duration of $t = 120$ s is $3.7 \mu\text{m}$. The corresponding thickness for IMC of solder using flux doped with 0.5 % NPs, is $2.89 \mu\text{m}$.
4. The growth kinetics of solders utilizing designated nanoparticles doped flux is dependent on “H^a” and “W^b”, where $a \approx 1$ and $b < 1$.
5. Finite element analysis has been utilized to model (i) the Cu diffusion into the geometrically altered solders during isothermal reflow at 523.15 K and (ii) heat transfer during air cooling stage. The results for concentration, temperature and velocity variables are utilized to discuss the occurrence of differential saturation rates, thermal gradients and velocity magnitudes on the specimens with different $\frac{2H}{W}$.

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References

1. S. Annur, R. Mahmoodian, M. Hamdi, and K.N. Tu. Intermetallic compounds in 3D integrated circuits technology: a brief review. *Sci. Technol. Adv. Mater.*, 18(1):1–11, 2017.
2. K.N. Tu, Yingxia Liu, and Menglu Li. Effect of Joule heating and current crowding on electromigration in mobile technology. *Applied Physics Review*, 4(1):011101, mar 2017.
3. C.C. Chang, Y.W. Lin, Y.W. Wang, and C.R. Kao. The effects of solder volume and Cu concentration on the consumption rate of Cu pad during reflow soldering. *Journal of Alloys & Compounds*, 492(1):99–104, 2010.
4. M.N. Islam, Ahmed Sharif, and Y.C. Chan. Effect of volume in interfacial reaction between eutectic Sn3.5Ag0.5 Cu solder and Cu metallization in microelectronic packaging. *Journal of Electronic Materials*, 34(2):143–149, 2005.

5. Luwei Liu and Mingliang Huang. Effect of solder volume on interfacial reactions between Sn3.5Ag0.75Cu solder balls and Cu pad. In *International Conference on Electronic Packaging Technology & High Density Packaging*, pages 299–304, 2010.
6. J. Shen and Y.C. Chan. Effect of metal/ceramic nanoparticle-doped fluxes on the wettability between Sn-Ag-Cu solder and a Cu layer. *Journal of Alloys & Compounds*, 477(1-2):909–914, 2009.
7. Shengyan Shang, Anil Kunwar, Yanfeng Wang, Xiao Qi, Haitao Ma, and Yunpeng Wang. Synthesis of Cu@Ag coreshell nanoparticles for characterization of thermal stability and electric resistivity. *Applied Physics A*, 124(7):492, jul 2018.
8. Shengyan Shang, Anil Kunwar, Yingchao Wu, and Haitao Ma. Effects of Cu nanoparticles doped flux on the microstructure of IMCs between Sn solder and Cu substrate. In *2017 18th International Conference on Electronic Packaging Technology (ICEPT)*, pages 1577–1581. IEEE, Aug 2017.
9. Andre Ribes and Christian Caremoli. Salome platform component model for numerical simulation. In *31st Annual International Computer Software and Applications Conference - Vol.2 - (COMPSAC 2007)*, pages 553–564, 2007.
10. M.J. Rizvi, H. Lu, and C. Bailey. Modeling the diffusion of solid copper into liquid solder alloys. *Thin Solid Films*, 517(5):1686–1689, 2009.
11. Anil Kunwar, Haoran Ma, Haitao Ma, Junhao Sun, Ning Zhao, and Mingliang Huang. On the increase of intermetallic compound's thickness at the cold side in liquid Sn and SnAg solders under thermal gradient. *Materials Letters*, 172:211–215, 2016.
12. Anil Kunwar, Bingfeng Guo, Shengyan Shang, Peter Raback, Yunpeng Wang, Jun Chen, Haitao Ma, Xueguan Song, and Ning Zhao. Roles of interfacial heat transfer and relative solder height on segregated growth behavior of intermetallic compounds in Sn/Cu joints during furnace cooling. *Intermetallics*, (93):186–196, 2018.
13. M. Malinen and P. Raback. *Multiscale Modelling Methods for Applications in Material Science, Chapter: Elmer finite element solver for multiphysics and multiscale problems*. Forschungszentrum Juelich, 2013.
14. Utkarsh Ayachit, Andy Bauer, Aashish Chaudhary, Dave DeMarle, Berk Geveci, Sebastien Jourdain, Kyle Lutz, Pat Marion, Robert Maynard, Nikhil Shetty, and Yumin Yuan. The ParaView Guide. Kitware. Inc., *ParaView*, 2008.
15. N. Cheung, Newton S. Santos, J. Quaresma, George S. Dulikravich, and Amauri Garcia. Interfacial heat transfer coefficients and solidification of an aluminum alloy in a rotary continuous caster. *International Journal of Heat and Mass Transfer*, 52(1-2):451–459, 2009.
16. Tomasz Gancarz, Zbigniew Moser, Wiadyslaw Gasior, Janusz Pstrus, and Hani Henein. A Comparison of Surface Tension, Viscosity, and Density of Sn and SnAg Alloys Using Different Measurement Techniques. *International Journal of Thermophysics*, 32(6):1210–1233, 2011.
17. Fatma Meydaneri, Mehmet Gunduz, Mehmet Ozdemir, and Buket Saatci. Determination of thermal conductivities of solid and liquid phases for rich-Sn compositions of Sn-Mg alloy. *Metals & Materials International*, 18(1):77–85, 2012.
18. Tomasz Gancarz, Wiadyslaw Gasior, and Hani Henein. Physicochemical Properties of Sb, Sn, Zn, and SbSn System. *International Journal of Thermophysics*, 34(2):250–266, 2013.
19. Haoran Ma, Anil Kunwar, Bingfeng Guo, Junhao Sun, Chengrong Jiang, Yunpeng Wang, Xueguan Song, Ning Zhao, and Haitao Ma. Effect of cooling condition and Ag on the growth of intermetallic compounds in Sn-based solder joints. *Applied Physics A*, 122(12):1–10, 2016.
20. Anil Kunwar, Julien Givernaud, Haoran Ma, Zhixian Meng, Shengyan Shang, Yunpeng Wang, and Haitao Ma. Modelling the Melting of Sn0.7Cu Solder Using the Enthalpy Method. In *Int. Conf. Electron. Packag. Technol.*, pages 166–169, Wuhan, China, 2016.
21. Sundman Bo, Xiao Gang Lu, and Hiroshi Ohtani. The implementation of an algorithm to calculate thermodynamic equilibria for multi-component systems with non-ideal phases in a free software. *Computational Materials Science*, 101:127–137, 2015.
22. Sundman Bo, U. Kattner, Mauro Palumbo, and S. Fries. OpenCalphad – a free thermodynamic software. *Integrating Materials & Manufacturing Innovation*, 4(1):1, 2015.

23. S.L. Tay, A.S.M.A. Haseeb, Mohd Rafie Johan, P.R. Munroe, and M.Z. Quadir. Influence of Ni nanoparticle on the morphology and growth of interfacial intermetallic compounds between Sn-3.8Ag-0.7Cu lead-free solder and copper substrate. *Intermetallics*, 33:8–15, 2013.
24. Y.H. Chan, M.M. Arafat, and A.S.M.A. Haseeb. Effects of reflow on the interfacial characteristics between Zn nanoparticles containing Sn3.8Ag0.7Cu solder and copper substrate. *Solder Surface Mounting Technology*, 25(2):91–98, 2013.
25. Yi Li and Y.C. Chan. Effect of silver (Ag) nanoparticle size on the microstructure and mechanical properties of Sn58BiAg composite solders. *Journal of Alloys & Compounds*, 645:566–576, 2015.
26. M.F. Arenas and V.L. Acoff. Contact angle measurements of Sn-Ag and Sn-Cu lead-free solders on copper substrates. *Journal of Electronic Materials*, 33(12):1452–1458, 2004.
27. Sushrut Bhanushali, Prakash Ghosh, Anuradda Ganesh, and Wenlong Cheng. 1D Copper Nanostructures: Progress, Challenges and Opportunities. *Small*, 11(11):1232–1252, 2015.
28. E. Saiz, A.P. Tomsia, N. Rauch, C. Scheu, M. Ruehle, M. Benhassine, D. Seveno, J. De Coninck, and S. Lopez-Esteban. Nonreactive spreading at high temperature: Molten metals and oxides on molybdenum. *Phys. Rev. E - Stat. Nonlinear, Soft Matter Phys.*, 76(4):1–15, 2007.
29. D.G.A.L. Aarts, H.N.W. Lekkerkerker, Hua Guo, G.H. Wegdam, and Daniel Bonn. Hydrodynamics of droplet coalescence. *Phys. Rev. Lett.*, 95(16):1–4, 2005.
30. Rajneesh Bhardwaj, J.P. Longtin, and Daniel Attinger. A numerical investigation on the influence of liquid properties and interfacial heat transfer during microdroplet deposition onto a glass substrate. *Internal Journal of Heat and Mass Transfer*, 50(15-16):2912–2923, 2007.
31. A.T.T. Tran, M.M. Hyland, Kentaro Shinoda, and Sanjay Sampath. Influence of substrate surface conditions on the deposition and spreading of molten droplets. *Thin Solid Films*, 519(8):2445–2456, 2011.
32. A.T.T. Tran, M.M. Hyland, Kentaro Shinoda, and Sanjay Sampath. Inhibition of molten droplet deposition by substrate surface hydroxides. *Surf. Coatings Technol.*, 206(6):1283–1292, 2011.
33. B. Silva, N. Cheung, Amauri Garcia, and J. Spinelli. Sn-0.7 wt%Cu-(xNi) alloys: Microstructure-mechanical properties correlations with solder/substrate interfacial heat transfer coefficient. *Journal of Alloys & Compounds*, 632:274–285, 2015.
34. Yongang Zhang, Steven Matthews, A.T.T. Tran, and Margaret Hyland. Effects of interfacial heat transfer, surface tension and contact angle on the formation of plasma-sprayed droplets through simulation study. *Surface Coatings Technology*, 307:807–816, 2016.
35. A.S.M.A Haseeb, Y.M. Leong, and M.M. Arafat. In-situ alloying of Sn-3.5Ag solder during reflow through Zn nanoparticle addition and its effects on interfacial intermetallic layers. *Intermetallics*, 54:86–94, 2014.
36. Fei Meng, Stephen A. Morin, Audrey Forticaux, and Song Jin. Screw dislocation driven growth of nanomaterials. *Acc. Chem. Res.*, 46(7):1616–1626, 2013.
37. A.M. Gusak and K.N. Tu. Kinetic theory of flux-driven ripening. *Phys. Rev. B - Condens. Matter Mater. Phys.*, 66(11):1–14, 2002.
38. J.F. Li, S.H. Mannan, M.P. Clode, D.C. Whalley, and D.A. Hutt. Interfacial reactions between molten Sn-Bi-X solders and Cu substrates for liquid solder interconnects. *Acta Mater.*, 54(11):2907–2922, 2006.
39. V.I. Dybkov. *Growth kinetics of chemical compound layers*. Cambridge Int Science Publishing, 1998.