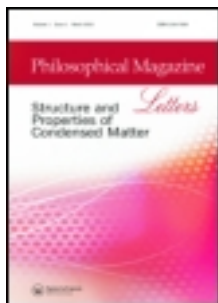


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Cu₃Sn suppression criterion for solid copper/molten tin reaction

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The formation of Cu₃Sn phase in the soldering reaction is believed to be harmful for the reliability of solder contacts on account of Kirkendall voiding in the compound. In this study, a criterion for the suppression of the growth of this phase by the fast growing scallop-like Cu₆Sn₅ compound is presented. The average thickness of the η-Cu₆Sn₅ phase above which the ε-Cu₃Sn phase starts to grow as a continuous layer at the Cu/Cu₆Sn₅ interface during liquid Sn/solid Cu interaction has been evaluated from thermodynamic and kinetic considerations.

Keywords: solid phase reactions; diffusion; thermodynamics; interfaces; soldering; phase competition

1. Introduction

Solders, substrate materials and their interfacial reaction products play crucial roles in the reliability of joint assemblies in microelectronic packages because they provide electrical, thermal and mechanical continuity in electronic assemblies [1,2]. Cu is the most common conductor metal utilized in contact with solders owing to its good solderability characteristics. Interaction between Sn-based liquid solders and Cu substrate leads to the formation, at the interface, of two intermetallic compounds (IMCs): a scallop-shaped η-Cu₆Sn₅ phase and a thin continuous layer of ε-Cu₃Sn phase [1,2]. The formation and growth of η-Cu₆Sn₅ and ε-Cu₃Sn IMCs greatly affects the physical properties and especially the mechanical properties of the joints. Indeed, because of the inherent brittle nature and the tendency to generate structural defects [3], very thick IMC layer at the solder/Cu interface may degrade the reliability of solder joints. Numerous studies indicated that excessive growth of IMCs may promote brittle failure through weakening the solder joint strength, and hence affecting its long-term reliability [4–7].

Moreover, studies of intermetallic formation between Cu- and Sn-based solders have shown that micro-voids can form at the Cu–Cu₃Sn interface and in the Cu₃Sn layer during annealing and aging of solder joints [8–14]. Development of such micro-voids in a solder joint is shown in Figure 1.

Given the fact that these Kirkendall voids are reported as a damaging factor leading to the weakening of the joint [8–10], initiating failures notably during thermal aging [4]

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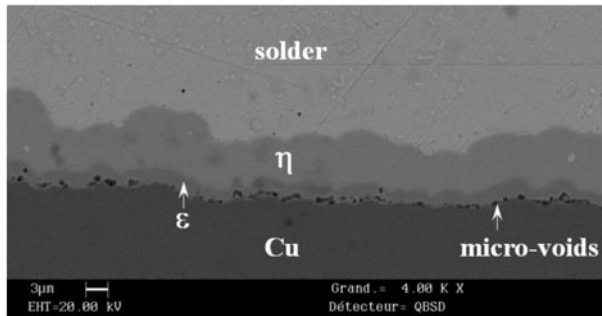


Figure 1. SEM micrographs of copper/solder interface showing voiding after annealing. Micro-voids developed at the Cu/ ϵ -Cu₃Sn interface and in the ϵ -Cu₃Sn layer during annealing of solder joint at 180 °C for 7 days.

it is advisable to avoid their formation. It is very important to underline that in almost all studies, the formation of Kirkendall voids in Sn-based solders/Cu substrate system is related to the formation of the ϵ -Cu₃Sn compound.

In the case of solid-state interactions between Sn-based solders and Cu substrates, the thickness of ϵ -Cu₃Sn layer is comparable to that of the η -Cu₆Sn₅ phase [4,15,16]. On the contrary, in liquid Sn-based solder/Cu systems the thickness of the Cu₃Sn phase is much lower than that of the Cu₆Sn₅ phase [5,17,18]. Note that most of the above referenced studies have not concentrated on the early stages of nucleation and growth of intermetallics in the liquid Sn/solid Cu system. For reactions times of some minutes, the size of Cu₆Sn₅ scallops reaches at least 4 μ m, followed by Cu₃Sn growth (see for example Ref. [18]). However, in a recent investigation, Lee et al. [19] studied the interfacial reaction of a Sn–3.0Ag–0.5Cu thin film during solder reflow for reaction times of 5–30 s and reflow temperatures of 230–260 °C. They reported that both ϵ -Cu₃Sn and η -Cu₆Sn₅ reaction layers are observed at the interface regardless of the reaction time. For example, after 30 s of reaction at 240 °C the average thicknesses of the ϵ and η layers are about 0.7 and 1.7 μ m, respectively.

The fact that the η -Cu₆Sn₅ phase grows faster than the ϵ -Cu₃Sn phase is due to the fact that during the reaction between molten solder and copper, the growth of Cu₆Sn₅ scallops takes place at the solder/metal interface by rapid liquid-state diffusion through nanometric liquid channels between the scallops, leading to a rapid growth rate of this phase [20,21]. Moreover, it is generally accepted that the first phase that forms and grows at the liquid solder/Cu interface is η -Cu₆Sn₅ and it is only afterwards that the growth of the ϵ -Cu₃Sn phase occurs at the Cu/Cu₆Sn₅ interface. However, to the best of our knowledge, the conditions under which the ϵ -Cu₃Sn phase starts to grow are not well known. We think that the growth conditions of the ϵ -Cu₃Sn are strongly related to mass flux balance at Cu/Cu₆Sn₅ interface and so to the thickness of the first η -Cu₆Sn₅ phase growing at this interface. The aim of this letter is to evaluate, from thermodynamic and kinetic considerations, the average thickness of the η -Cu₆Sn₅ phase above which ϵ -Cu₃Sn starts to grow as a continuous layer at the Cu/Cu₆Sn₅ interface during liquid Sn/solid Cu interaction.

2. Model

In our case, diffusion through the Cu/Cu₃Sn interface is not a growth-rate controlling process [22]. As a first approximation, we assume that liquid channels (with average thickness δ) exist between the mono-sized hemispherical scallops (with radius R) of the growing η -Cu₆Sn₅ phase (see Figure 2a). Also we assume that a ϵ -phase layer of some minimal constant thickness l_{cr} (say $l_{cr} \sim 2$ nm) has just formed by nucleation and lateral growth and now is trying to grow normally between the η -phase and the Cu. It seems physically evident that the ϵ -phase (as any other phase) cannot be thinner than, say, a nanometer (owing to nucleation issues or/and the existence of a minimal size of an elementary cell within the structure of Cu₃Sn).

We shall not discuss the details of nucleation and lateral growth of the ϵ -phase since the voiding in this phase seems to have become a problem only after the formation of a continuous layer. All we need to know now is under what conditions can the thinnest layer of this phase be stopped by being kinetically suppressed by the fast-growing η -phase? In other words we wish to evaluate the scallop size R^* of the η -phase at which the ϵ -phase layer will start to grow.

We assume that the liquid is homogeneous in concentration and already saturated by copper for $x > R$ and that a constant concentration gradient exists in the liquid phase

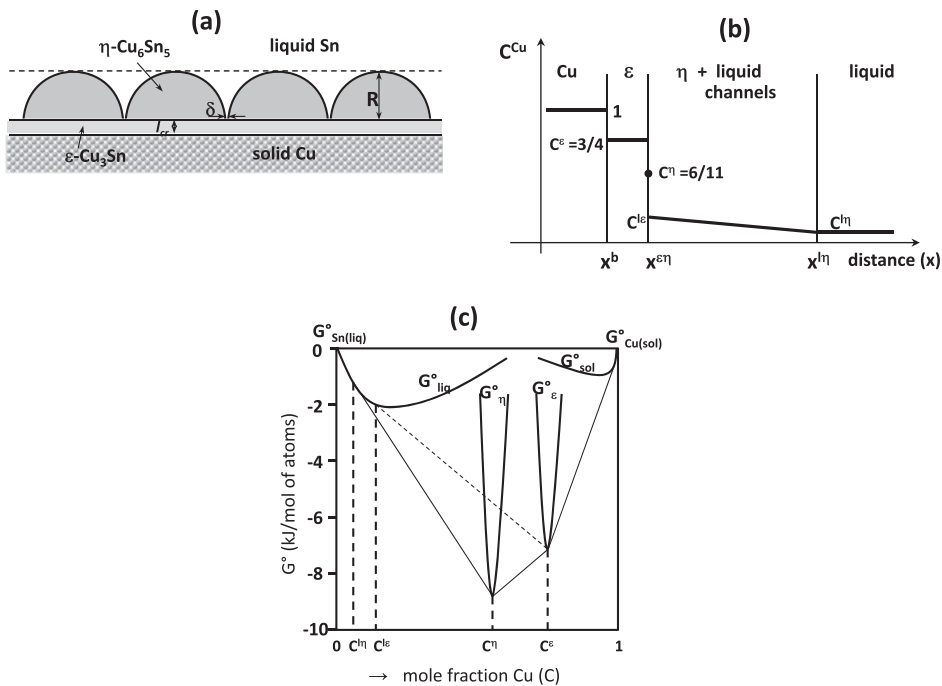


Figure 2. Model system: (a) Schematic morphology of η -Cu₆Sn₅ phase formed at the solid Cu/liquid Sn interface and (b) schematic presentation of variation of Cu concentration through the solid Cu/liquid Sn system. (c) Schematic presentation of variation of the Gibbs free-energy formation of (Sn,Cu) liquid phase, (Cu,Sn) solid phase and η -Cu₆Sn₅ and ϵ -Cu₃Sn compounds at $T=523$ K indicating the stable equilibria (—) and the metastable liquid/ ϵ equilibrium (---). References states: stable states at 523 K (pure liquid Sn and pure solid Cu) [23,24].

(channels) from the top of the liquid/ η interface ($x=x^{\text{ln}}$), where the copper concentration corresponds to the liquid/ η equilibrium concentration (c^{ln}), to the ε/η interface at the bottom of the channels ($x=x^{\text{en}}$), where the copper concentration in the liquid channels corresponds to the liquid/ ε metastable equilibrium (c^{le}) condition – see Figure 2b.

For the fluxes of Cu atoms (number of atoms per unit area per unit time) through both intermetallic phases (evidently, through the ε -phase layer and the liquid channels) we can use the following expressions [22]:

$$\Omega J^{(\varepsilon)} = \frac{\tilde{D}^{(\varepsilon)} \Delta c_{\varepsilon}^{\text{eq}}}{l_{cr}}, \quad (1)$$

$$\Omega J^{(\eta)} = D_{\text{Cu}}^{\text{melt}} \frac{c^{l/\varepsilon} - c^{l/\eta}}{R} \frac{S^{\text{free}}}{S^{\text{total}}} = \frac{\delta}{R^2} D_{\text{Cu}}^{\text{melt}} (c^{l/\varepsilon} - c^{l/\eta}), \quad (2)$$

where Ω is an atomic volume, $\tilde{D}^{(\varepsilon)} \Delta c_{\varepsilon}^{\text{eq}}$ is the integrated diffusion coefficient in the ε – phase, $D_{\text{Cu}}^{\text{melt}}$ is the diffusion coefficient of Cu in the liquid Sn–Cu solution, $c^{l/\varepsilon}$ and $c^{l/\eta}$ are the equilibrium concentrations of Cu at the liquid/ ε – phase and liquid/ η – phase interface correspondingly (see Figure 2c). According to the constraint that the interface between the scallops and Cu is occupied completely by scallops except in the thin channels, we have $N\pi R^2 \approx S^{\text{total}} = \text{constant}$, where N is the number of scallops. The free surface (the cross-sectional area of channels at the bottom) for the supply of Cu from the substrate is $S^{\text{free}} = 2\pi RN(\delta/2) = (\delta/R)S^{\text{total}}$, where δ is the channel width. Note that the number of liquid channels per unit area of reaction interface (proportional to $S^{\text{free}}/S^{\text{total}} = \delta/R$) is higher for a scallop-form η -phase compared to a semispherical-form η -phase. The error in the value of δ/R can be estimated to be the a/h ratio (about 20–30%) where, a and h are the average values of the base radius and the height of a η -scallop, respectively ($a = h = R$ in the case of a semispherical-form).

Both planar solid interfaces, Cu/ ε and ε/η , and the averaged non-planar (scallop-like) interface η/melt will shift accordingly to the following growth laws:

$$\begin{aligned} (1 - c^{\varepsilon}) \frac{dx^{\text{Cu}/\varepsilon}}{dt} &= 0 - \frac{\tilde{D}^{(\varepsilon)} \Delta c_{\varepsilon}^{\text{eq}}}{l_{cr}^{\varepsilon}}, \\ (c^{\varepsilon} - c^{\eta}) \frac{dx^{\varepsilon}/\eta}{dt} &= \frac{\tilde{D}^{(\varepsilon)} \Delta c_{\varepsilon}^{\text{eq}}}{l_{cr}^{\varepsilon}} - \frac{\delta D_{\text{Cu}}^{\text{melt}}}{R^2} (c^{l/\varepsilon} - c^{l/\eta}), \\ (c^{\eta} - 0) \frac{dx^{\eta}/\text{Sn}}{dt} &= \frac{\delta D_{\text{Cu}}^{\text{melt}}}{R^2} (c^{l/\varepsilon} - c^{l/\eta}) \end{aligned} \quad (3)$$

Eventually, the growth rate of the ε -phase layer can be expressed as the difference in the velocities of the two interfaces $\left(\frac{d\Delta x^{\varepsilon}}{dt} = \frac{dx^{\varepsilon}/\eta}{dt} - \frac{dx^{\text{Cu}/\varepsilon}}{dt}\right)$:

$$\frac{d\Delta x^{\varepsilon}}{dt} \Big|_{l_{cr}} = \left(\frac{1}{c^{\varepsilon} - c^{\eta}} + \frac{1}{1 - c^{\varepsilon}}\right) \frac{\tilde{D}^{(\varepsilon)} \Delta c_{\varepsilon}^{\text{eq}}}{l_{cr}^{\varepsilon}} - \frac{1}{c^{\varepsilon} - c^{\eta}} \frac{\delta D_{\text{Cu}}^{\text{melt}}}{R^2} (c^{l/\varepsilon} - c^{l/\eta}), \quad (4)$$

Finally, the growth condition of the ε -phase layer becomes:

$$\frac{1}{R^2} \frac{1}{c^{\varepsilon} - c^{\eta}} \delta D_{\text{Cu}}^{\text{melt}} (c^{l/\varepsilon} - c^{l/\eta}) < \frac{1 - c^{\eta}}{(c^{\varepsilon} - c^{\eta})(1 - c^{\varepsilon})} \frac{\tilde{D}^{(\varepsilon)} \Delta c_{\varepsilon}^{\text{eq}}}{l_{cr}^{\varepsilon}}, \quad (5)$$

$$R > R^* = \sqrt{\frac{(c^{l/\varepsilon} - c^{l/\eta})(1 - c^\varepsilon)}{1 - c^\eta} \frac{D_{\text{Cu}}^{\text{melt}}}{\tilde{D}^{(\varepsilon)} \Delta c_\varepsilon^{\text{eq}}} \delta \times l_{\text{cr}}^\varepsilon} \quad (6)$$

For an estimate of exact values of R^* we need to find values of $c^{l/\varepsilon}$, $c^{l/\eta}$, $D_{\text{Cu}}^{\text{melt}}$ and $\tilde{D}^{(\varepsilon)} \Delta c_\varepsilon^{\text{eq}}$. It is generally accepted that $D_{\text{Cu}}^{\text{melt}} = 10^{-9} \text{m}^2/\text{s}$. In their recent work Paul et al. [15] measured experimentally the value of the integrated diffusion coefficients for the ε -phase (the product $\tilde{D}^{(\varepsilon)} \Delta c_\varepsilon^{\text{eq}}$) in the range 498–623 K. At 523 K, $\tilde{D}^{(\varepsilon)} \Delta c_\varepsilon^{\text{eq}} = 0.87 \times 10^{-16} \text{m}^2 \text{s}^{-1}$.

To find the equilibrium concentration of Cu at the liquid/ ε – phase and the liquid/ η – phase interfaces we used CALPHAD data to build the $G_f(c)$ dependence (in J/mole) in Figure 3 in the form of G – $H\text{SER}$ [23].

$$G_l(c_{\text{Sn}}) = c_{\text{Sn}} G_l^{\text{Sn}} + (1 - c_{\text{Sn}}) G_l^{\text{Cu}} + RT(c_{\text{Sn}} \ln(c_{\text{Sn}}) + (1 - c_{\text{Sn}}) \ln(1 - c_{\text{Sn}})) + c_{\text{Sn}}(1 - c_{\text{Sn}})(Lf_0 + (2c_{\text{Sn}} - 1)Lf_1 + (2c_{\text{Sn}} - 1)^2 Lf_2), \quad (7)$$

where G_l^{Sn} , G_l^{Cu} are the Gibbs free energies for pure liquid Sn and pure liquid Cu, given by the following expressions:

$$G_l^{\text{Sn}} = 9496.31 - 9.809114T - 8.2590486T \ln(T) - 0.016814429T^2 + 2.623131 \times 10^{-6}T^3 - 1081244/T,$$

$$G_l^{\text{Cu}} = 5194.277 + 120.973331T - 24.112392T \ln(T) - 2.65684 \times 10^{-3}T^2 + 0.129223 \times 10^{-6}T^3 + 52478/T - 5.849 \times 10^{-21}T^7. \quad (8)$$

The energetic components are taken from the thermodynamic assessment of Shim et al. [24]:

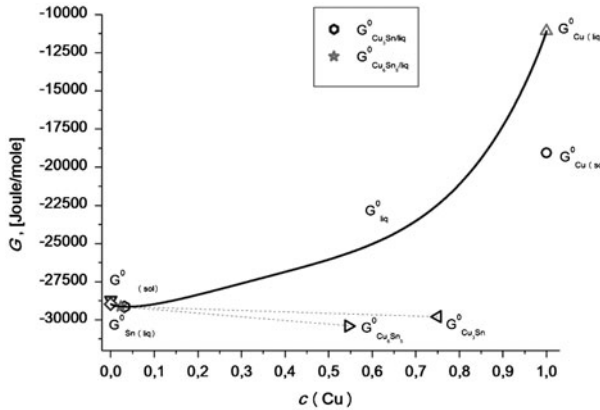


Figure 3. Thermodynamics of Cu–Sn system. Calculated variation of the Gibbs free-energy of formation (G^0) of (Cu,Sn) liquid phase as a function of molar fraction of Cu (c^{Cu}). Gibbs free-energy of formation for ε - Cu_3Sn and η - Cu_3Sn_5 compounds and pure solid Cu. Reference states G-HSER: FCC_A1(Cu) and BCT_A5(Sn) at 298.15 K [23,24].

$$\begin{aligned} Lf_0 &= 9002.8 - 5.8381T, \\ Lf_1 &= 20100.4 + 3.6366T, \\ Lf_2 &= 10528.4. \end{aligned} \quad (9)$$

Reference states were FCC_A1 (Cu) and BCT_A5 (Sn) at 295.15 K.

We take the relations for the Gibbs potentials of the stoichiometric phases as [24]:

$$G^\eta = -6869.5 - 0.1589T + 0.545G_s^{\text{Cu}} + 0.455G_s^{\text{Sn}},$$

and

$$G^\varepsilon = -8194.2 - 0.2043T + 0.75G_s^{\text{Cu}} + 0.25G_s^{\text{Sn}}, \quad (10)$$

where the relations for the Gibbs free energy of the solid Sn and Cu are given as:

$$\begin{aligned} G_s^{\text{Cu}} &= 7770.458 + 130.485235T - 24.112392T \ln(T) - 0.00265684T^2 \\ &\quad + 1.29223 \times 10^{-7}T^3 - 52478/T, \end{aligned}$$

and

$$\begin{aligned} G_s^{\text{Sn}} &= 2524.724 + 4.005269T - 8.2590486T \ln(T) - 0.016814429T^2 \\ &\quad + 2.623131 \times 10^{-6}T^3 - 1081244/T - 1.2307 \times 10^{25}T^9. \end{aligned} \quad (11)$$

Application of Equations (10) and (11) gives at $T=523$ K

$$\begin{aligned} G^\eta &= -30412.3 \text{ J/mole}, \\ G^\varepsilon &= -29784.2 \text{ J/mole}. \end{aligned}$$

Figure 3 gives the calculated variation of the Gibbs free energy of formation (G°) of the (Cu, Sn) liquid phase as a function of molar fraction of Cu, as well as the Gibbs free energy for the formation of the ε -Cu₃Sn and η -Cu₃Sn₅ compounds and pure solid Cu.

By simple calculation, using the common tangent rule (see Figure 3), we find the values $c^{l/\varepsilon} = 0.03152$ and $c^{l/\eta} = 0.02277$.

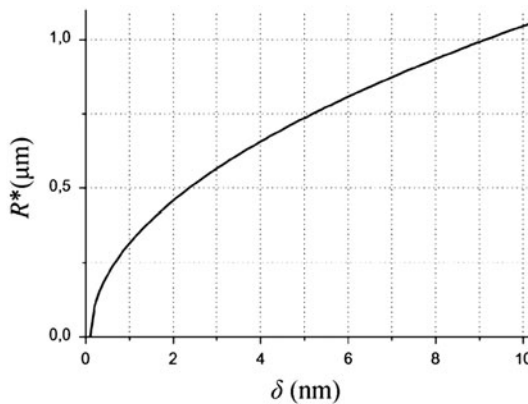


Figure 4. Variation of the crossover η -scallop size (R^*) as a function of liquid channels size (δ) inside the η phase – see Equation (6).

After substitution of all parameters into Equation (6) we can build the dependence $R^*(\delta)$ (see Figure 4). According to Jong-Ook Suh et al. [25] the width of the channel was estimated to be about 2.5 nm which gives the value $R^* \approx 0.6 \mu\text{m}$.

In principle, details of the channel parameters should be found from the conditions of optimal non-equilibrium steady-state wetting in open system under competition between the tendency to complete wetting and the tendency to transform the liquid channel into the intermetallic phase by reaction. We hope to solve this problem in the future.

3. Conclusion

Our crude evaluations predict that the $\varepsilon\text{-Cu}_3\text{Sn}$ phase layer can overcome suppression by the $\eta\text{-Cu}_6\text{Sn}_5$ phase when the mean size of the scallops exceeds about $1 \mu\text{m}$. Immediately after this we can expect the beginning of voiding on account of the difference of mobilities in ε -phase. A more general condition, taking into account the nucleation stage, will be considered separately in the framework of nucleation in open systems [26,27].

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