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Possibility of a shape phase transition for solidification of tin at scallop-like surfaces of Cu_6Sn_5

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The possibility of solder-spreading transitions in solidification of solder at a rough rigid intermetallic surface is proven theoretically. Depending on the misorientation of scallops on the interface, one can observe a two-dimensional spreading transition over the scallops or a one-dimensional spreading transition along the triple-junction of two intermetallic compound scallops and liquid solder. The extent of undercooling can be determined not only by different interface energies, but by different angles between neighbouring scallops as well.

Keywords: nucleation; phase transformations; wetting; thermodynamics; undercooling

Fabrication of integrated circuits includes numerous reflows of solder–copper contacts. The most used lead-free solders in the microelectronic industry are Sn–Ag–Cu alloys [1]. Each reflow starts from melting of solder, continues by fast growth of scallops of Cu_6Sn_5 and ends with solidification of unreacted molten solder. Recent experimental studies [2–5] mainly focused on the effect of the solder size and of the metallic solid in contact with the liquid solder on the undercooling behaviour, demonstrating that undercooling can be as high as a few tens of degrees even for solder balls with some hundreds of micrometres in diameter. However, to the best of our knowledge, there are no studies in the literature devoted to the theoretical aspects of nucleation in a solder ball in contact with a reactive substrate. Attention is almost always paid to the reaction stage [6–10], given the fact that interfacial reactivity can affect the physical properties of the interface and especially the mechanical behaviour of the system. In this article, we concentrate on the last stage of reflow, i.e. the solidification over the scallop-like interface of liquid Sn with Cu_6Sn_5.

Firstly, the undercooling of the molten solder at this stage can effectively increase the reaction time between solid and liquid, so it is important to evaluate the nucleation barrier. Secondly, the most probable nucleation places may influence the morphology of solidified solder, and the morphology can be important for the mechanical properties of

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*Corresponding author. Email: fhodaj@simap.grenoble-inp.fr the joint. After reflow, the initial Cu/solder interface is transformed onto Cu/Cu_3Sn-ε/Cu_6Sn_5-η/solder interfaces. Thus, the liquid solder is in contact with scallops of Cu_6Sn_5 compound. Since Ag does not react with Cu, we can simplify the problem by considering that the solder alloy contains only Sn.

We can distinguish at least three nucleation mechanisms of solidification:

(1) Homogeneous (in the bulk).
(2) On the nearly flat part of the η/Sn interface.
(3) At the junction of the scallops and a grain boundary (GB) – perhaps the most interesting one.

1. Homogeneous nucleation

Homogeneous nucleation is well described and implies the following.

The change in Gibbs free energy during formation of a spherical nucleus of radius r and containing n atoms is given by

$$\Delta G = -\Delta g n + \gamma_{sl} 4\pi r^2 = -\Delta g n + \gamma_{sl} 4\pi r_0^2 n^{2/3} \tag{1}$$

$$\Omega_{at} n = \frac{4}{3}\pi r^3 \Rightarrow r = \left(\frac{3\Omega_{at}}{4\pi}\right)^{1/3} n^{1/3} \equiv r_0 n^{1/3},$$

where $r_0 = \left(\frac{3\Omega_{at}}{4\pi}\right)^{1/3}$

The critical size is $r_{cr} = \frac{2\gamma_{sl}\Omega_{at}}{\Delta g}$ and the nucleation barrier is given by

$$\Delta G^{*}_{\text{homo}} = \frac{16\pi}{3}\,\Omega_{at}^2\,\frac{\gamma_{sl}^3}{\Delta g^2}, \tag{2}$$

where γ_{sl} is a solid/liquid surface tension and Ω_{at} the atomic volume. The driving force for the phase transformation, Δg, depends on the degree of undercooling $\Delta T = T_m - T$, and is given by

$$\Delta g(\Delta T) = \frac{q}{T_m}\Delta T$$

where q is the latent heat of melting per atom and T_m is the equilibrium melting temperature.

2. Heterogeneous nucleation on the flat molten Sn/Cu_6Sn_5 interface

Figure 1 schematically represents the nucleation of a spherical cup of tin at the Sn/Cu_6Sn_5(η-phase) interface in two cases: contact angles θ lower and higher than 90°.

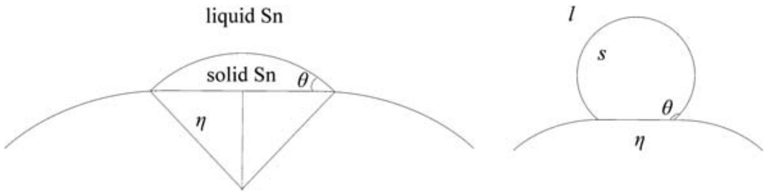

Figure 1. Nucleation of solid tin at the flat part of a Cu_6Sn_5 scallop (η phase).

If $-1<(\gamma_{l\eta}-\gamma_{s\eta})/\gamma_{sl}<1$, then $\cos\theta=(\gamma_{l\eta}-\gamma_{s\eta})/\gamma_{sl}$, otherwise $\theta=0$ or $\theta=\pi$. $\gamma_{l\eta}$ and $\gamma_{s\eta}$ are the liquid tin/η and solid tin/η interfacial tensions, respectively.

Standard calculations lead to the following expression for the ratio of nucleation barriers,

$$\frac{\Delta G^*_{\text{hetero}}}{\Delta G^*_{\text{homo}}}=\frac{2-3\cos\theta+\cos^3\theta}{4}. \tag{3}$$

Note that all equations are valid for $\theta<\pi/2$ as well as for $\theta>\pi/2$.

Three limiting cases can be distinguished:

(a) $\theta\to 0\Rightarrow\dfrac{\Delta G^*_{\text{hetero}}}{\Delta G^*_{\text{homo}}}\to 0;$

In this case there is 2D-spreading of the solid phase; solid tin wets the scallop ($\gamma_{ls}+\gamma_{s\eta}<\gamma_{l\eta}$), making the nucleation barrier tend to zero and thus making undercooling impossible.

(b) $\theta\to\frac{\pi}{2}\Rightarrow\dfrac{\Delta G^*_{\text{hetero}}}{\Delta G^*_{\text{homo}}}\to\dfrac{1}{2};$

In this case nucleation is favourable, but the barrier is still significant.

(c) $\theta\to\pi\Rightarrow\dfrac{\Delta G^*_{\text{hetero}}}{\Delta G^*_{\text{homo}}}\to 1;$

This limiting case seems natural since the nuclei do not like the compound surface as the nucleation site and thus only homogeneous nucleation becomes possible.

3. Nucleation at the joint of two scallops and a grain boundary

We take the nucleus as a "slice" of solid tin in the form of a "curved prism" with two flat lateral faces and one cylindrical surface (length l, radius of curvature r – see Figure 2). The shape ratio ($\varphi=l/\rho$) should be optimized at each volume (number of atoms in the nucleus).

According to elementary geometry (Figure 2)

$$\begin{cases}\varepsilon=\frac{\pi}{2}-\theta,\\ \beta+\varepsilon=\alpha\end{cases}\Rightarrow\beta=\theta+\alpha-\frac{\pi}{2} \tag{4}$$

where, additionally to equilibrium conditions for angle θ, one more equilibrium condition exists *before* solidification at the joint:

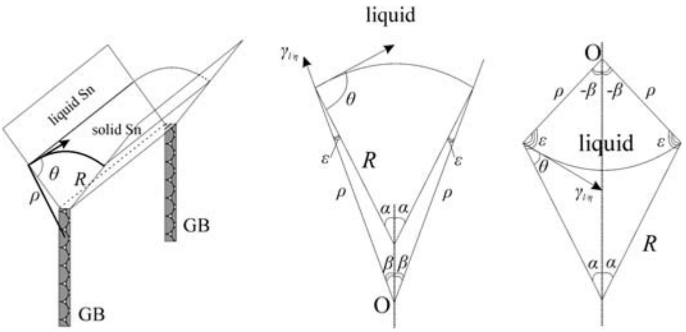

Figure 2. (a) Geometry of nucleation at the triple joint solid/η interface-solid/η interface-grain boundary; (b) centre of curvature (O) at the solid side ($\beta > 0$ and $\theta > \pi/2 - \alpha$); (c) centre of curvature at the liquid side ($\beta < 0$ and $\theta < \pi/2 - \alpha$).

$$2\gamma_{l\eta}\cos\alpha = \gamma_{gb}. \tag{5}$$

There is still some doubt on whether or not full wetting of grain boundaries occurs between grains of the compound by liquid tin. In the case of full wetting ($2\gamma_{l\eta} < \gamma_{gb}$, [11]) one has liquid channels between scallops going all the way to the substrate or to the Cu_3Sn thin layer. In the case of partial wetting [12], a compromise was suggested by Jong-ook-Suh et al. [13], namely full wetting between scallops growing at the base of neighbouring Cu grains, and partial wetting between scallops based on the same Cu grain and therefore having a small misorientation.

Here, we consider possible nucleation of solid tin at the triple joint with partial wetting, $\frac{\gamma_{gb}}{2\gamma_{l\eta}} < 1$. The total surface energy, which should be optimized, is given by

$$W^{\mathrm{surf}}(n,\varphi) = 2\gamma_{ls}S^{\mathrm{base}} + \gamma_{ls}S^{\mathrm{top}} + 2(\gamma_{s\eta} - \gamma_{l\eta})S^{\mathrm{side}} = 2\gamma_{ls}\left(S^{\mathrm{base}} + \frac{S^{\mathrm{top}}}{2} - S^{\mathrm{side}}\cos\theta\right) \tag{6}$$

Elementary geometrical considerations, for example for the case $\beta > 0$, imply

$$S^{\mathrm{base}} = \frac{1}{2}R^2 2\beta - 2.\frac{1}{2}R\rho\sin\varepsilon = R^2\beta - R\rho\cos\theta, \tag{7}$$

$$\frac{R}{\sin(\pi - \alpha)} = \frac{\rho}{\sin\beta} \Rightarrow R = \rho\frac{\sin\alpha}{\sin\beta},$$

so that

$$S^{\mathrm{base}} = \rho^2\frac{\sin\alpha}{\sin\beta}\left(\beta\frac{\sin\alpha}{\sin\beta} - \cos\theta\right). \tag{8}$$

One can easily check by direct derivation that, in case of $\beta < 0$ $(\theta + \alpha < \frac{\pi}{2})$, the expression for S^{base} remains formally the same and positive (the first term becomes negative and the second term positive). Note that in this case the centre of curvature appears over the top.

$$S^{\text{top}} = (R \cdot 2\beta) \cdot l = (\varphi\rho)\left(\rho\frac{\sin\alpha}{\sin\beta}\right) \cdot 2\beta = \varphi\rho^2 2\beta\frac{\sin\alpha}{\sin\beta},$$

$$S^{\text{side}} = \rho l = \varphi\rho^2.$$

Thus, we can consider the surface energy as a function of linear size parameter ρ and of shape parameter $\varphi = l/\rho$.

$$W^{\text{surf}}(\rho,\varphi) = 2\gamma_{ls}\rho^2\left\{\frac{\sin\alpha}{\sin\beta}\left(\beta\frac{\sin\alpha}{\sin\beta} - \cos\theta\right) + \varphi\beta\frac{\sin\alpha}{\sin beta} - \varphi\cos\theta\right\}$$

By introducing the notation

$$\psi = \frac{\sin\alpha}{\sin\beta}\left(\beta\frac{\sin\alpha}{\sin\beta} - \cos\theta\right), \tag{9}$$

the expression for W^{surf} becomes

$$W^{\text{surf}}(\rho,\varphi) = 2\gamma_{ls}\rho^2\psi\left(1 + \frac{\sin\beta}{\sin\alpha}\varphi\right)$$

The parameters (ρ, φ and ψ) are linked by the constraint of volume (the number of atoms multiplied by the atomic volume): $n\Omega_{at} = S^{\text{base}}l = \varphi\rho \cdot \rho^2\frac{\sin\alpha}{\sin\beta}(\beta\frac{\sin\alpha}{\sin\beta} - \cos\theta) = \varphi\rho^3\psi$, leading to $\varphi = \frac{n\Omega_{at}}{\rho^3\psi}$, so that

$$W^{\text{surf}}(n,\rho(\varphi)) = 2\gamma_{ls}\rho^2\psi\left(1 + \frac{\sin\beta}{\sin\alpha}\frac{n\Omega_{at}}{\rho^3\psi}\right) = 2\gamma_{ls}\psi\left(\rho^2 + \frac{\sin\beta}{\sin\alpha}\frac{n\Omega_{at}}{\psi}\frac{1}{\rho}\right) \tag{10}$$

The minimization of $W^{\text{surf}}(n,\varphi)$ over φ (or ρ) at fixed n leads to

$$\rho_{\text{opt}} = n^{1/3}\Omega_{at}^{1/3}\left(\frac{1}{2\psi}\frac{\sin\beta}{\sin\alpha}\right)^{1/3}, \quad \varphi_{opt} = \frac{n\Omega_{at}}{\rho_{\text{opt}}^3\psi} = 2\frac{\sin\alpha}{\sin\beta}.$$

Clearly the expression for φ_{opt} applies only for $\beta = \alpha + \theta - \frac{\pi}{2} > 0$ (or $\theta > \pi/2 - \alpha$). When β tends to zero, the optimal shape parameter tends to infinity. When β becomes negative, expression (10) for the surface energy as a function of the inverse of ρ becomes monotonic (see Figure 3a).

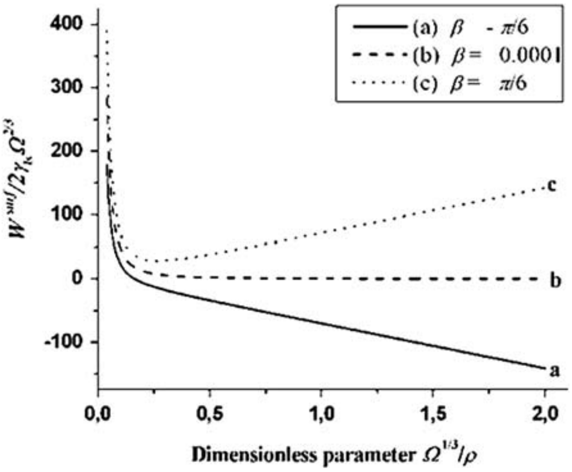

Figure 3. Minimization of the surface energy over dimensionless parameter $\Omega^{1/3}/\rho$ for $\alpha = \pi/4$, $n = 100$ and $\beta = -\pi/6$ (a); $\beta = 10^{-4}$ (b); $\beta = \pi/6$ (c).

Thus, with negative and zero values of β, nuclei of solid Sn will tend to spread almost as a line along the junction scallop 1 – scallop 2 grain boundary. Of course, in this case one can introduce at least one more factor – the line tension of the junction, which will make the infinite line impossible and of course the curvature radius ρ cannot be less than the atomic size – see below.

Inserting the values of φ_{opt} and ρ_{opt} in Equation (10), the expression for W^{surf} becomes

$$\begin{aligned} W^{\text{surf}}(n_{\text{opt}}, \varphi_{\text{opt}}) &= 2\gamma_{ls}\psi\left(\frac{n^{2/3}\Omega_{at}^{2/3}\sin\beta}{2\sin\alpha\cdot\psi}\right)^{2/3}\left(1+\frac{\sin\beta}{\sin\alpha}\cdot\frac{\sin\alpha}{\sin\beta}\right) \\ &= \left(\frac{3}{2\pi}\right)^{1/3}\gamma_{ls}n^{2/3}\Omega_{at}^{2/3}\psi^{2/3}\left(\frac{\sin\beta}{\sin\alpha}\right)^{2/3}, \end{aligned}$$

with ψ given by Equation (9) and by introducing the notation $\tilde{\gamma} = \left(\frac{3}{2\pi}\right)^{1/3}\gamma_{ls}(\beta - \frac{\sin\beta}{\sin\alpha}\cos\theta)^{1/3}$,an expression for W^{surf} as a function of the number of atoms, n, in the nuclei is obtained:

$$W^{\text{surf}}_{\text{optimized}} = \tilde{\gamma}\,4\pi r_0^2 n^{2/3},$$

Thereby, the change in Gibbs free-energy during the formation of a nucleus (depending on the values of α and β) is

$$\Delta G^{*}_{gb} = \Delta g n(\tilde{\gamma}\,4\pi\pi_0^2)n^{2/3}, \tag{11}$$

From Equations (1), (2) and (11) we deduce the nucleation barrier:

$$\Delta G^{*}_{gb} = \frac{16\pi}{3}\frac{\Omega^{2}_{at}}{\Delta g^{2}}\tilde{\gamma}^{3}. \tag{12}$$

A comparison of ΔG_{gb}, ΔG_{homo} and ΔG_{hetero} gives

(i) If $\beta \equiv \alpha + \theta - \pi/2 > 0$ $(\theta > \pi/2 - \alpha)$:

$$\frac{\Delta G^{*}_{gb}}{\Delta G^{*}_{\text{homo}}} = \left(\frac{\tilde{\gamma}}{\gamma_{sl}}\right)^{3} = \frac{3}{2\pi}\left(\beta - \frac{\sin\beta}{\sin\alpha}\cos\theta\right),$$

$$\frac{\Delta G^{*}_{gb}}{\Delta G^{*}_{\text{hetero}}} = \frac{\frac{\Delta G^{*}_{gb}}{\Delta G^{*}_{\text{homo}}}}{\frac{\Delta G^{*}_{\text{hetero}}}{\Delta G^{*}_{\text{homo}}}} = \frac{\frac{3}{2\pi}\left(\beta - \frac{\sin\beta}{\sin\alpha}\cos\theta\right)}{\frac{2-3\cos\theta+\cos^{3}\theta}{4}} = \frac{6}{\pi}\frac{\beta - \frac{\sin\beta}{\sin\alpha}\cos\theta}{2 - 3\cos\theta + \cos^{3}\theta},$$

with $\cos\theta = \sin(\alpha - \beta)$,

(ii) If $\beta \equiv \alpha + \theta - \pi/2 \leqslant 0$ $(\theta \leqslant \pi/2 - \alpha)$:

$$\frac{\Delta G^{*}_{gb}}{\Delta G^{*}_{\text{homo}}} = 0,$$

$$\frac{\Delta G^{*}_{gb}}{\Delta G^{*}_{\text{hetero}}} = 0,$$

where:

$$\cos\theta = \frac{\gamma_{l\eta} - \gamma_{s\eta}}{\gamma_{sl}}, \quad \cos\alpha = \frac{\gamma_{gb}}{2\gamma_{l\eta}}.$$

So, in the heterogeneous nucleation of a solid phase at the rough substrate, one may observe not one, but at least two spreading transitions:

(1) If $\frac{\gamma_{l\eta}-\gamma_{s\eta}}{\gamma_{sl}} \geqslant 1$, then solid tin wets compound scallops and spreads over them, so that solidification proceeds without any undercooling.
(2) If $\alpha < \frac{\pi}{2} - \theta$, $(\frac{\gamma_{l\eta}-\gamma_{s\eta}}{\gamma_{sl}} > \sin\alpha)$, then one obtains a one-dimensional spreading transition: solid tin wets the joint and spreads along it, so that, again, solidification proceeds without any undercooling.

Comparing cases 1, 2 and 3, we can predict that the joint of scallops helps solid tin to spread (at least in 1D).

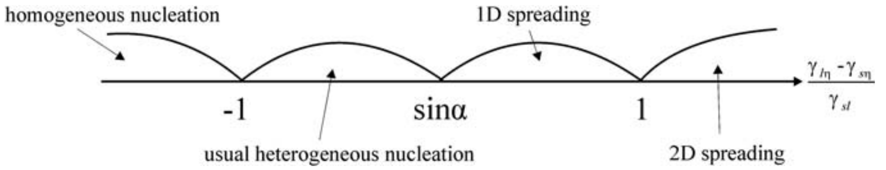

Figure 4. Phase fields (schematic presentation).

We can identify four phase fields (see Figure 4):

(i) $\frac{\gamma_{l\eta}-\gamma_{s\eta}}{\gamma_{sl}} \geqslant 1$ – two-dimensional (2D) spreading, zero barrier.

(ii) $1 > \frac{\gamma_{l\eta}-\gamma_{s\eta}}{\gamma_{sl}} \geqslant \sin\alpha$ $(\theta \leqslant \pi/2 - \alpha)$ – one-dimensional (1D) spreading, zero barrier.

(iii) $\sin\alpha > \frac{\gamma_{l\eta}-\gamma_{s\eta}}{\gamma_{sl}} > -1$ $(\pi/2 - \alpha < \theta < \pi)$ – usual activated heterogeneous nucleation.

(iv) $-1 > \frac{\gamma_{l\eta}-\gamma_{s\eta}}{\gamma_{sl}}$ $(\theta = \pi)$ – homogeneous nucleation.

Varying the angle between scallops by choosing couples with different misorientation, one may try to observe the phase shape transition. Note that the linear size cannot be less than the atomic size, $\rho_{\min} = a$.

Note also that the shape parameter will be limited, i.e. it will not go to infinity:

$$\varphi_{\max} \frac{n\Omega_{at}}{\rho_{\min}^3 \Psi} \approx \frac{n\Omega_{at}}{a^3 \Psi(\beta \to 0)} \approx \frac{n\Omega_{at}}{a^3 \sin\alpha\cos\alpha} \approx \frac{n}{\sin\alpha\cos\alpha}$$

In this limiting transition, it is important to take into account that $\cos\theta = \sin(\alpha - \beta)$, and then to develop a series in respect to the parameter β.

For $n = 100$ atoms and values of $\alpha = 30$ and 45°, $\varphi_{\max}$ are about 230 and 200 respectively, i.e. $l_{\max}$ about 10 nm.

To summarize, considering the nucleation on the rough surfaces, we found the theoretical possibility of a one-dimensional spreading transition along the grooves at the triple-junction of two solid–liquid rigid interfaces and a grain boundary.

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