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On the mechanism of the binary Cu/Sn solder reaction

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The solder reaction of Cu and molten pure Sn is studied by scanning and transmission electron microscopy. Similar as reported for SnPb solder, the intermetallic Cu_6Sn_5 product is formed in a scallop-like morphology and a growth kinetic proportional to the cube root of time is found. Size distributions and shape of the scallops are determined experimentally. Comparing the binary reaction couple Cu/Sn with the technical combination Cu/SnPb, a significant difference in the length to width aspect ratio of individual scallops is noticed. We demonstrate by transmission electron microscopy that neighbored scallops are not separated by channels of solder, but by grain boundaries. Thus, grain boundary transport is the rate controlling step and the observed variation in scallop shape is due to differences in the interface tensions of the two reaction couples. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1852724]

During the last thirty years the integration density of electronic devices increased continuously. Solder technology has to go conform with this progress. In recent flip chip technology[1] even several thousand connections per chip may be obtained. To increase the density of packaging, a size reduction of solder joins is an important goal. However, a further miniaturization is hindered by the fast growth of the intermetallic Cu_6Sn_5 phase, which on the one hand warrants good adhesion but on the other hand causes severe embrittlement. Understanding the reaction mechanisms and developing strategies to slow down the reaction rate are of enormous relevancy to flip chip technology.

Among other combinations, the ternary Cu/SnPb solder system has been frequently investigated.[2–4] During the reaction of solid Cu with liquid SnPb solder, Cu_6Sn_5 intermetallic grows in a scallop-like morphology, which allows fast atomic transport through channels of molten solder (diffusion coefficient in the melt $D \approx 10^{-5}$ cm^2/s). Some authors claim that the channels are stabilized by lead, which does not take part in the reaction.[3] Others assume that the nonplanar growth is just due to the increased reduction rate of free energy achieved this way,[1,2] but most likely, channels are stabilized by boundary contributions to the energy balance. Recently, Gusak and Tu presented a kinetic model[5] assuming that the scallops, separated by molten channels, grow in a self-similar manner, so that the total interface area stays constant. The eventual formation of Cu_3Sn is neglected. This model is able to describe the cube root kinetics typically observed in solder reactions and furthermore it yields a definite prediction of the size distribution of the scallops.

This experimental work concentrates on the reaction of the binary system Cu/Sn in order to focus on basic reaction mechanisms. A few experiments were repeated with eutectic SnPb solder for comparison. During the reaction, Cu substrates polished to a roughness of Sn 0.25 μm were immersed in flux heated to $\approx$245 °C and afterwards quenched to room temperature immediately. Subsequently, specimens were cut by spark erosion and prepared for cross section-, surface-, and TEM-analysis. In order to resolve scallops by scanning electron microscopy (SEM), specimens were etched for 1 min in a 5% HCl and 95% methanol mixture, so that unreacted tin was removed.

In Fig. 1 the reaction zone of the binary system is shown in plane (viewing direction normal to the interface) and cross-section view (viewing direction along original interface). It is clearly seen that also the binary system develops a nonplanar morphology of the Cu_6Sn_5 product, with channels of solder apparently extending to the Cu substrate. Thus, it is obvious that Pb is not a required ingredient for scallop-type growth.

SEM images were evaluated to determine the growth kinetics. Average lateral scallop width and their normal height are plotted separately in Fig. 2. To determine the width from plane-view images, each scallop was approximated by a circle of identical area. Within the limits of error, both microstructural parameters develop according to the same kinetics with a growth exponent close to $1/3$ as predicted by Gusak's model. In consequence, the aspect ratio, i.e, width to height, stays approximately constant during the reaction. For Cu/Sn we determine this aspect ratio to $\rho = 2.8 \pm 0.3$, while for the ternary system Cu/SnPb we find ρ

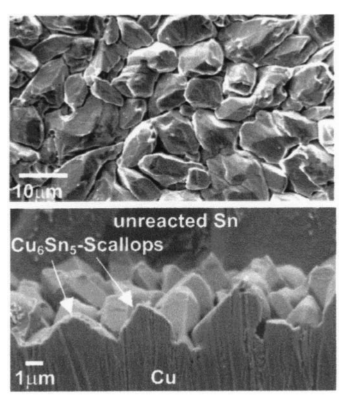

FIG. 1. Scanning electron microscopy: (top) plane view image of a Cu/Sn reaction zone after 8 min reflow., (bottom) cross-section image of a Cu/Sn reaction after 4 min reflow.

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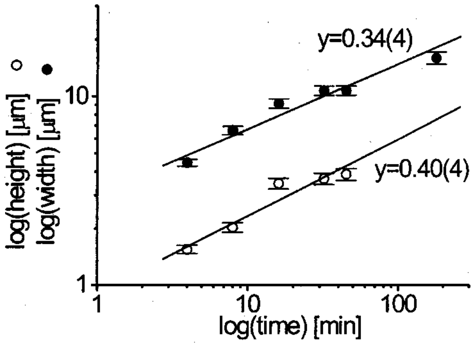

FIG. 2. Scallop growth with annealing time. Lateral width (from plane view images) and height (from cross section images) are evaluated separately.

=1.2. Thus, there is a remarkable difference in the morphology. In the binary system scallops appear much broader and shorter than in the case of Cu/SnPb.

Since the characteristics of the reaction in the binary system seem to agree with Gusak's assumptions,[5] we determine size distributions of the scallops. For that, only plane-view images should be used, since opposed to cross section images no geometric correction is needed. Experimental size distributions obtained after different reaction times are compared with Gusak's prediction in Fig. 3. Since a kinetics proportional to $t^{1/3}$ points at first hand to conventional ripening, the size distribution of Lifshitz, Slyozov, and Wagner[6,7] is also plotted in one case for comparison.

Although the average radius increases by a factor of about three during the stages shown, the experimental distributions do not vary significantly, which confirms a self-similar ripening of the morphology. The matching between experimental data and Gusak's distribution is not perfect, e.g., histograms appear broader and more symmetrically but nevertheless, it is clearly seen that the model of nonconservative ripening yields a much better description than the classical LSW theory of ripening.

Most studies about scallop growth published yet, are based on scanning electron microscopy. However, potential preparation artifacts introduced by etching, suggest to check

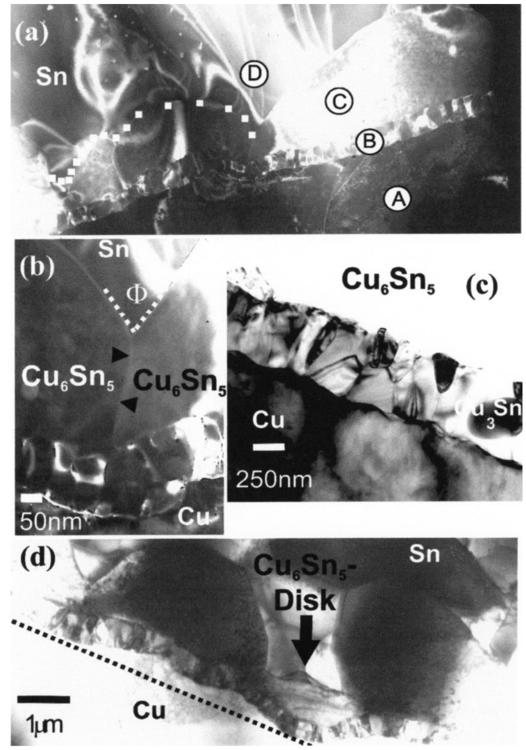

FIG. 4. TEM micrographs of a Cu/Sn specimen after 4 min reflow.

the present interpretation of scallop growth by independent transmission electron microscopy. For that, after the solid/liquid reaction was fixed by quenching, suitable cross sections of the reaction zone were prepared by ion milling. Different phases were identified by EDX. In Fig. 4(a) a binary reaction couple after 4 min annealing is shown. Four different regions are easily distinguished: the Cu-substrate (A), the Cu_3Sn layer (B), a Cu_6Sn_5 grain/scallop (C), and the unreacted tin (D). Most remarkable, the channels between individual scallops reveal a sharpness down to about $\delta = 1$ nm [Fig. 4(b)]. Furthermore, a clearly defined triple joint with wetting angle Φ is seen. Since the appearance of the triple joints does not depend on the reflow time and thus on the

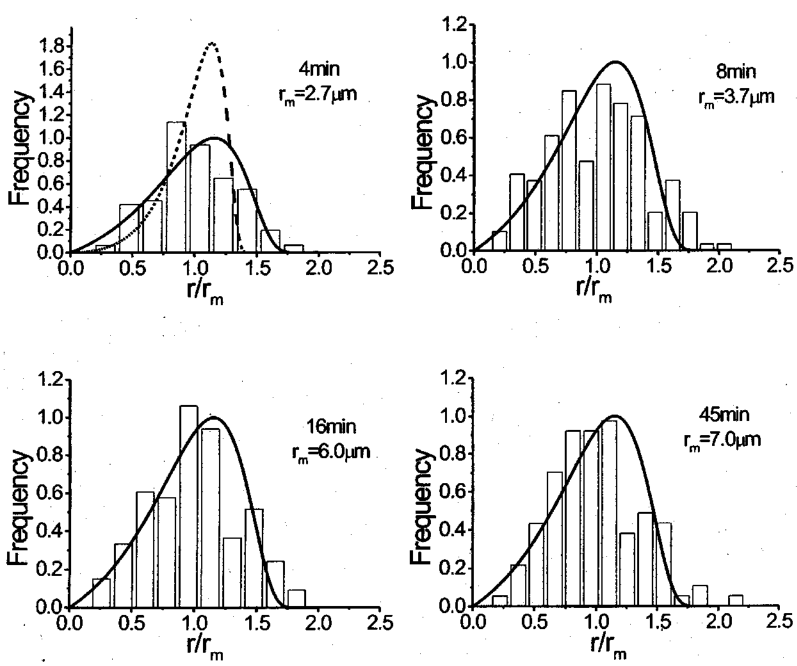

FIG. 3. Experimental size distributions (histograms) in comparison to Gusak's prediction (solid line). For the stage after 4 min reflow the classical LSW distribution is shown also (dashed line).

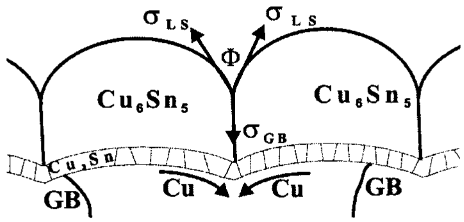

FIG. 5. Schematic of the solid/liquid interreaction zone.

scallop size, it is suggested that the observed wetting angle is an equilibrium feature at the reaction temperature instead of being formed at quenching. In consequence, those channels must be interpreted as ordinary grain boundaries separating two grains of Cu_6Sn_5. Potentially, the much thicker molten channels postulated in previous work are an artifact of the etching needed to obtain sufficient contrast for SEM.

Between the scallops and the Cu substrate a polycrystalline Cu_3Sn layer has formed, 300 nm in thickness [Fig. 4(c)]. In contrast to previous SEM work and its interpretation by Gusak's model, this layer seems to form just at the beginning of the reaction, as we can detect it in TEM micrographs after only 10 s annealing with a thickness of already 115 nm. The dense Cu_3Sn layer consists of a row of columnar grown grains. However, with its high density of grain boundaries it is probably not the rate limiting factor for the Cu supply to the reactive solid/liquid interface.

We cannot observe any correlation between the scallop structure and the grain boundary structure of the underlying Cu substrate. Thus, grain boundaries of Cu can be excluded as preferential nucleation sites. During the reaction, the substrate develops a certain waviness in correspondence to the scallop structure. The onset of this process is already noticed in the presented pictures [Fig. 4(d)]. This confirms that Cu is predominantly transported along the Cu_6Sn_5 grain boundaries. The outflow of Cu cannot be compensated by volume diffusion inside the Cu substrate or by diffusion along the interfaces to the Cu_3Sn layer. In consequence the region close to the Cu_6Sn_5 GBs shifts into the Cu substrate. Also the ripening process can be observed in Fig. 4(d). Due to the Gibbs–Thomson effect a small scallop has already shrunk to a thin disk. In the SEM these leftovers of a former scallop may be overlooked, as they are destroyed during the preparation, and erroneously a broad channel is indicated. The observed characteristics of the reaction zone are summarized in the schematics of Fig. 5.

We proved the same features at the ternary Cu/SnPb system. Again after 10 s, a fine-grained Cu_3Sn layer appears in a thickness of about 60 nm. Also in this case the channels between the scallops turn out to be grain boundaries. Only the wetting angle Φ at the grain boundaries is significantly smaller, so that the scallops are elongated normal to the interface.

The presented TEM observations have two important consequences: (i) The shape of the scallops is controlled by the equilibrium of the tensions at the triple junction between the grain boundary and the solid/liquid interfaces (see Fig. 5) according to

$$\cos\frac{\varphi}{2} = \frac{\sigma_{\mathrm{GB}}}{2\cdot\sigma_{\mathrm{LS}}}, \tag{1}$$

where Φ is the wetting angle, σ_{GB} the grain boundary energy, and σ_{LS} the interface energy between scallop and melt. Obviously σ_{LS} for Sn is higher than σ_{LS} for SnPb, since Φ is significantly larger for the binary reaction. Indeed the higher interface energy for the binary system has to be expected because of the higher melting point of pure Sn in comparison to the eutectic SnPb alloy. (ii) GB transport of Cu must be taken into account when the kinetics is discussed quantitatively. Probably, this is the rate controlling step. The use of the triple product[8] $\overline{D}=s\delta D_{\mathrm{GB}}$ does not change the principle of Gusak's model. Regarding the conservation of mass, we find again a cube root kinetics

$$c_i dV = c_i\frac{2}{3}\rho dR = J dt = \frac{2\overline{D}\Delta c}{\rho R^2}dt, \tag{2}$$

$$\Rightarrow R^3 = kt \ \mathit{with}\ k := 9\overline{D}\frac{\Delta c}{c_i}\frac{1}{\rho^2}, \tag{3}$$

where c_i, V, J, and $\Delta c \approx 0.01$ are the mole fraction of Cu in Cu_6Sn_5, the scallop volume per unit area, the total Cu current, and the concentration variation across the Cu_6Sn_5 layer, respectively. From Fig. 2 we find $k = 1.5\times10^{-19}\ \mathrm{m}^3/\mathrm{s}$, which requires a grain boundary diffusion of $D_{\mathrm{GB}} = 5\times10^{-10}\ \mathrm{m}^2/\mathrm{s}$, close to values for bulk melts. However, considering that the bulk diffusion[9] of Cu_6Sn_5 amounts already to $10^{-13}\ \mathrm{m}^2/\mathrm{s}$ at 513 K , such a value of grain boundary diffusion seems to be in the possible range. This all the more as recent diffusion studies by Herth *et al.*[10] have demonstrated that wetted grain boundaries, although structurally different from liquid channels, may have a diffusivity near to that of the bulk melt.

The insight by TEM indicates a potential lever to reduce the growth rate of the intermetallic. Sputtering a Cu_6Sn_5 layer as "under bulb" metallization on Cu substrates, annealing it to obtain a coarse grained microstructure and selecting a solder distinguished by a high interfacial energy to Cu_6Sn_5 might be a promising strategy to reduce the scallop length and the transport rate of Cu.

[1] K. N. Tu and K. Zeng, Mater. Sci. Eng., R. **34**, 1 (2001).
[2] H. K. Kim, H. K. Liou, and K. N. Tu, Appl. Phys. Lett. **66**, 2337 (1995).
[3] H. K. Kim and K. N. Tu, Phys. Rev. B **53**, 16027 (1996).
[4] K. N. Tu, T. Y. Lee, J. W. Jang, L. Li, D. R. Frear, K. Zeng, and J. K. Kivilahti, J. Appl. Phys. **89**, 4843 (2001).
[5] A. M. Gusak and K. N. Tu, Phys. Rev. B **66**, 115403 (2002).
[6] V. V. Slezov, *Theory of Diffusion Decomposition of Solid Solution* (Harwood Academic, Dordrecht, 1995).
[7] C. Wagner, Z. Elektrochem. **65**, 581 (1961); **65**, 485 (1961).
[8] I. Kaur, Fundamentals of Grain and Interphase Boundary Diffusion, 1989.
[9] H. Mehrer, *Landoldt-Börnstein, Diffusion in Solid Metals and Alloys* (Springer Berlin, 1990).
[10] S. Herth, F. Ye, M. Eggersmann, O. Gutfleisch, and R. Würschum, Phys. Rev. Lett. **92**, 095901 (2004).