Movement of solder fillers because of the unevenness of interfacial tension in self-organization assembly process

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Abstract. Soldering or anisotropic conductive adhesives (ACAs) are used for assembling of devices with high-density area-array terminals. However, solder bump processes are high-cost and interconnects of ACAs are less-reliable. The purpose of this study is to develop a novel method. Self-organization assembly method that uses active resin containing solder fillers may allow reliable interconnects at low-cost. Fundamental process of Self-organization assembly are movement, coalescence, and wetting of molten fillers in resin. The focus of this paper is on the movement of fillers. In-situ observations of coalescence behavior for 40\(\mu\)m\(\phi\) molten fillers in the resin revealed irregular movement of the fillers at a velocity of several \(\mu\)m/s. Numerical analysis, using improved volume fraction method, indicated that a 10\% degradation of interfacial energy on one side of a 40\(\mu\)m\(\phi\) filler could move the filler at a velocity of several mm/s. This degradation of the interfacial energy was resulted the remaining oxide film.

1. Introduction
Most of highly-integrated electronic components with narrow-pitch area-array terminals are assembled by solder bumps formed by printing. However, the process designs need tries and errors [1]. A high accuracy for voids is also required [2]. On the other hand, the interconnects using ACAs are not reliable because the conductivity depends on only mechanical contacts [3].

Figure 1 shows schematic diagrams of Self-organization assembly method [4]. As shown in (a), resin containing solder fillers was supplied between components and substrates allover the terminal patterns. The melting point (m.p.) of the solder was lower than curing temperature (\(T_c\)) of the resin. The temperature was controlled between the m.p. and the \(T_c\), as shown in (b). Solder fillers then move, coalesce with each other and are transported to the wettable terminals. The resultant conductive pathways are shown in (c) and they are similar to solder bumps in morphology. Reheating at higher than the \(T_c\) made the resin underfill. Interconnects formed in this low cost process, as for ACAs, may achieve high reliability and high degree of flexibility against design change of devices or substrates.

Figure 1. Schematic views of Self-organization assembly process. (a) supplied resin containing solder particles, (b) movement, coalescence, and wetting of particles, (c) formed conductive paths.
Fundamental processes of Self-organization assembly at temperatures higher than the m.p. of the solder are movement, coalescence, and wetting of molten fillers. In-situ observation of filler coalescence were carried out. These observations clarified the irregular movement of fillers in the active resin that led to coalescence and wetting. The focus of this paper is on this movement of the fillers. The unevenness of interfacial tension that was involved in the elimination of the oxide films were evaluated by a numerical study as the possible mechanism of the movement.

2. Materials
Eutectic Sn-Bi spherical particles were used as the material to produce a conductive path. The m.p. of Sn-Bi solder is 138 °C. Average particle sizes of the solder fillers used in this study was 10 or 40 µm φ. A newly developed thermosetting epoxy resin was used as a container for the fillers. Temperature characteristics of the resin viscosity were measured. To simulate the actual temperature change from assembly experiments the temperature was held at 150 °C. The resin begins to cure in a few minutes after the solder melts. A carboxylic acid contained in the resin as the curing agent acts as an activator to eliminate the oxide film around the fillers.

3. In-situ observations of fillers movement

3.1. Experimental procedure
Figure 2 shows the instruments used for in-situ observations on filler movement. Resin containing 10 vol%, 40 µm φ fillers was used. To eliminate filler wetting effects, cover glasses of low wettability were used. 100 µm φ stainless wires were cramped between two cover glasses together with the resin as spacers. Transmitted light through a hole in a metal plate enabled clear observations.

Figure 3 shows a typical heating profile. Before heating to 145 °C to melt the fillers, a pre-heating treatment to eliminate oxides around fillers at 80 °C was carried out for 4 min.

3.2. Results and discussions
Figure 4 shows the trajectory of a typical filler. Figure 5 shows the temporal change of the coalescence frequency with a blue line. This frequency was measured by the shrinkage in the filler number in sight per unit time. Figure 5 shows also the velocity of the filler focused in figure 4, by a red line. Heating was started at t=0 s and the measurement interval was Δt=1 s as shown in both figures.

From t=0 s to t=460 s, at which time the m.p. of the solder was reached, movement of the fillers was hardly observed. At the m.p. of the solder neighboring fillers began to coalesce. This coalescence induced flow in the resin and induced further coalescences. However, by t=466 s, this movement ceased. The reason for this is that as the distance between fillers increased because of coalescence...
further coalescence became difficult. From approximately \( t=500 \) s, the fillers showed irregular movement at a velocity of several \( \mu \text{m/s} \). The fillers showed repeat of aggregation and separation from the clusters. Figure 4 shows active filler movement through some congestions. As the coalescence frequency was low until \( t=525 \) s, this active movement could not have been caused by coalescence. After \( t=525 \) s, the frequency of the coalescence increased again. This increase is thought to be due to fillers movement which was not caused by coalescence when the oxides around the fillers eliminated enough.

Figure 4. Trajectory of a solder filler.

Figure 5. Coalescence frequency of solder fillers and velocity of a filler.

4. Clarification of fillers movement mechanism

The concentration gradient, Brownian movement, and heat convection were discussed as possible mechanisms of filler movement. These are popular mechanism of particle movement in fluids. These mechanisms do not depend on whether the particles are solids or liquids. Since the fillers hardly moved before melting these mechanisms are not plausible as the mechanism of filler movement in this study.

A self-running mechanism for oil droplets in water with added surfactant [5] has been reported. This phenomenon was thought to be caused by an unevenness of interfacial energy around a droplet due to chemical Marangoni effect. It is well-known that the fillers have deep scars on the surface resulted from sieve classification. Unevenness of the interfacial energy around molten filler on this system was thought to be caused by the thickness distribution of oxide films.

Quantification of the unevenness of interfacial energy was attempted using a numerical study based on fluid dynamics. The mass conservation law and the momentum conservation law were analyzed through an improved Volume of Fluid (VOF) method [6]. To model the unevenness using the Continuum Surface Force (CSF) model [7], the interfacial energy of the filler in the resin was defined as interfacial tension in the following equation:

\[
\gamma = \begin{cases} 
\gamma_0 & \text{(at } x < x_g) \\
\gamma_0 - \Delta\gamma & \text{(at } x > x_g) 
\end{cases}
\]  

(1)

Where \( \gamma_0 \) is interfacial tension between the bare solder and the resin, \( \Delta\gamma \) is the degradation of the interfacial tension because of oxides on the filler and \( x_g \) is an \( x \)-coordinate of the center of gravity for the filler. Under the assumption that the density of the solder is constant, \( x_g \) can be obtained by the following equation:

\[
x_g = \left( \frac{1}{\int_{x_{min}}^0 x \rho \, dx} \left( \int_{x_{min}}^0 \rho \, dx \right) \right) \left( \int \sum_{n=1}^N VOF(n) \right) \left( \int \sum_{n=1}^N VOF(n) \right)
\]

(2)

Where \( n \) is element number and \( VOF(n) \) is the VOF ratio of the solder at \( n \)th element.

A 40 \( \mu \text{m} \) droplet of molten solder was positioned in the resin. This model, as shown in Figure 6 (a), simulates the filler when the oxides on the left half of the filler are eliminated. The unevenness of the interfacial tension makes the static fluid pressure in the left half of the filler higher than that in the right half. The density and the viscosity of the resin are \( 1.2 \times 10^3 \) kg/m\(^3\) and \( 1.0 \times 10^{-1} \) Pa s, respectively.
The density and the viscosity of the solder are $8.5 \times 10^3$ kg/m$^3$ and $1.8 \times 10^{-3}$ Pa s, respectively. The interfacial tension between the bare molten solder and the resin, $\gamma = 5.7 \times 10^{-1}$ [N/m].

Figure 6 shows the behavior of the filler movement at $\Delta \gamma = 0.5 \gamma_0$. The filler moved to the right without much deformation. Figure 7 quantitatively shows effects of the unevenness of the interfacial tension. $x_1$ represents the rightmost side of the filler and $x_2$ represents the leftmost side. At higher $\Delta \gamma$, when simulating the fillers with a thicker oxide film on the right half, the filler moved faster. Even the filler of $\Delta \gamma = 0.1 \gamma_0$ moved at a velocity of several mm/s which is much faster than the movement of the observed fillers. The unevenness of interfacial tension is thought to be a plausible mechanism for filler movement in the resin.

**Figure 6.** Analysis results on effects of interfacial tension distribution, $\Delta \gamma = 0.5 \gamma_0$.

**Figure 7.** Quantitative evaluation on effects of interfacial energy unevenness.

5. Conclusion
The focus of this study was to determine the fundamental processes and mechanism of the Self-organization assembly process for the movement of fillers in resin. Based on the in-situ observation of the movement of many molten fillers in an active resin, the unevenness of the interfacial energy around a filler and other phenomena are quantitatively discussed as a plausible. The following results were obtained from this study.

Through in-situ observations of the coalescence behavior of the fillers in a resin, irregular movements of the fillers at a velocity of several $\mu$m/s after melting were observed. Before melting, the fillers hardly moved.

The numerical studies using an improved VOF method, revealed that a 10% degradation of the interfacial tension at the right half of the filler can move the filler at a velocity of several mm/s.

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