Formulation of percolating thermal underfills using hierarchical self-assembly of micro- and nanoparticles by centrifugal forces and capillary bridging

Thomas Brunschwiler, Gerd Schlottig, Songbo Ni, Yu Liu, Javier V. Goicoechea, Jonas Zürcher, and Heiko Wolf
IBM Research – Zurich, 8803 Rüschlikon, Switzerland, tbr@zurich.ibm.com, +41 44 724 86 81.

ABSTRACT

Thermal underfills are crucial to support integration density scaling of future integrated circuit packages. Therefore, a sequential process using hierarchical self-assembly of micro- and nanoparticles is proposed to achieve percolating thermal underfills with enhanced particle contacts. The three main process steps hereby are assembly of filler particles by centrifugation, formation of nanoparticle necks by capillary bridging, and the backfilling of the porous structure with an unfilled capillary adhesive.

Numerical simulations predicting trajectories and distributions of micron-sized particles dispensed into a rotating disk are presented. The trajectories exhibit a strong dependence on the particle size; thus in the case of polydisperse filler particles nonuniform particle beds may result. An efficient centrifugal disk design with spiral-like guiding structures is experimentally validated. Defect-free, percolating particle beds in confined space with fill fractions of 46 vol-% to 66 vol-%, i.e., close to the theoretical limit, are also presented.

The self-assembly of nanoparticles, forming enhanced thermal contacts between the percolating filler particles, is discussed. Two consecutive evaporation patterns during the capillary bridging process were identified: 1) dendritic network growth and 2) collapse of capillary bridges. The concave neck topology could only be achieved at temperatures below the boiling point. An optimal evaporation temperature of 60°C with respect to in-plane uniformity and neck shape was identified. Existing thermal gradients normal to the cavity surface resulted in strongly asymmetric neck formation in the cavity. Hence, uniform heating in an oven is the preferred method to initiate evaporation. Two types of bi-modal dielectric necks are demonstrated. Polystyrene acts as the adhesive between thermally conductive alumina particles to form mechanically stable dielectric necks after an annealing step at 140°C. Interstitial and core-shell necks are presented.

Finally, a benchmark study was performed to compare the effective thermal conductivity of the percolating thermal underfill with and without necks with state-of-the-art capillary underfills. A close to fivefold improvement could be obtained for diamond filler particles with silver necks (3.8 W/m-K).

KEYWORDS: Percolating thermal underfill, sequential processing, hierarchical self-assembly, centrifugation, capillary bridging, neck formation

INTRODUCTION

Efficient heat dissipation in packages of integrated circuits (ICs) is essential to support the integration-density and performance scaling of future systems [1-5]. Heat conduction through the solder interface into the laminate at low thermal gradients would allow the elimination of the backside heat sink, enabling thin form-factor Flip-Chip-on-Board (FCOB) packages suitable for mobile applications (Fig. 1a). High-performance 3D chip stacks also require a low thermal interface resistance of the solder interfaces within the chip stack to relax the system design constraints imposed by excessive thermal gradients (Fig. 1b).

In both applications, a major heat-removal bottle-neck is the solder ball array interface between die and laminate or individual dies, when using traditional packaging materials [6, 7]. The space between the solder balls (denoted here as cavity) is traditionally filled with a capillary underfill, composed of silica spheres dispersed in an adhesive matrix, to mitigate mechanical stress concentrations and therefore improve mechanical reliability [8]. Several publications now propose to substitute the silica particles with dielectric particles with improved thermal conductivity, such as alumina, silicon carbide, aluminum nitride (22-40, 120, 160 W/m-K instead of 1.2 W/m-K) [9, 10, 11]. So far, only moderate improvements of the effective thermal conductivities of about 1 W/m-K have been reported. This is due to the rapid increase of underfill viscosity at particle loadings above the percolation threshold (> 25 vol-% [11, 12]). The capillary pressure would be too low to allow such
underfills to penetrate the cavity. Hence, the heat dissipation in nonpercolating thermal underfills is hampered by the poor particle-to-particle contact, which constitutes itself as an adhesive layer between individual particles.

The particle-to-particle interface dominates even for highly filled, hence percolating, thermal interface materials, which are squeezed between the package and the heat sink. The point contact between particles results in a heat flux concentration, causing large local thermal gradients [13, 14, 15].

In this publication, we report on a novel sequential process to form percolating thermal underfills with enhanced thermal particle-to-particle contact by means of hierarchical self-assembly of micro- and nano-sized particles using centrifugation and capillary-bridging. In the first section, the sequential process is introduced, followed by a section describing the self-assembly of micron-sized particles by centrifugation and the neck formation by capillary-bridging. Finally, we conclude with a thermal benchmarking of the novel process.

**SEQUENTIAL PROCESSING ENABLING HIERARCHICAL SELF-ASSEMBLY OF ENHANCED PERCOLATING THERMAL UNDERFILLS**

We propose a sequential process methodology with an additional degree of freedom to form enhanced percolating thermal underfills, as compared to the single-step process used for pre-formulated capillary underfills. The sequence contains the following process steps:

1) **Centrifugation**: A percolating particle bed within the cavity of the package is achieved by the self-assembly of micron-sized, thermally conductive filler particles using centrifugal forces (Fig. 2, panel 1).

2) **Neck formation**: Improved particle-to-particle contacts, so-called necks are achieved through the self-assembly of nanoparticles by capillary-bridging in the second step (Fig. 2, panel 2). Liquid connections with the shape of such necks between micron-sized particles were observed and studied in wet sand [16]. The liquid connections, referred to as capillary bridges, occur for water contents below the available space between the solid particles and are a result of minimization of surface free-energy between the liquid, the solid, and the gas phase. Vakarelsk et al. [17] proposed the use capillary bridging of suspensions of dispersed metallic nanoparticles, followed by the evaporation of the carrier fluid, to achieve a self-assembled electrically conductive mesh on a substrate. We propose to use the same concept to achieve improved thermal contacts between the filler particles themselves and the filler particles and substrates by injection of dielectric nanosuspensions into the percolating filler-particle bed. The nanoparticle concentration in the suspension increases steadily during the subsequent evaporation step. Finally, nanoparticles remain and form the enhanced thermal contacts called necks (between filler particles) and collars (between filler particles and substrates), see Fig. 3.

3) **Backfilling**: A particle-free capillary underfill is finally dispensed along the chip etch to penetrate the particle bed including the necks, completing the sequential underfill composite (Fig. 2, panel 3) as discussed in [7].

**FILLER-PARTICLE SELF-ASSEMBLY BY CENTRIFUGATION**

The self-assembly of filler particles by viscous drag has already been demonstrated [7]. The micron-sized particles were suspended in water and pumped through the cavities with a filter placed at their outlet. The method yielded high particle loadings of 40 to 60 vol-% in the confined space.

However, the associated pressure drop to drain the liquid through the evolving particle bed limits the dynamics of the process. Accordingly, only small chip footprints (≤ 1 cm²) and particle diameters larger than 30 µm are currently possible. They are not suitable for cavities in a 3D chip stack whose height is less than 30µm.

We propose the use of centrifugal forces to assemble dry filler particles as depicted in Figs. 4 and 5 to overcome those limitations. Multiple FCOB or chip-stack modules are placed
into pockets of a rotating disk. A cover plate with a central opening and guiding structures allow particle dispensing, support uniform filling, and prevent particles from leaving the cavities. Controlled particle dispensing is achieved through the tilting angle of the particle-filled syringe. The syringe is connected to a rotating eccentric mass, which is actuated by an electric motor. The rotating mass induces vibrations resulting in a continuous particle feed.

**Figure 4:** Cross section of centrifugal disk showing the self-assembly of filler particles into cavities of FCOB modules by centrifugal forces. Filler particles are dispensed by a syringe through the central feed.

**Figure 5:** Isometric view of the rotating disk with a capacity of four modules. Four different guiding structures were implemented to identify the most efficient cover design in the experiment.

An efficient centrifugal filling of the cavities depends on the design of the guiding structures and the arrangement of the modules. To determine those geometries, knowledge of the filler-particle trajectories is necessary. In this study, we used COMSOL to perform numerical two-dimensional (2D) kinetic models in the disk reference system (particle motion relative to the rotating disk). Gravitational forces and particle collisions with the top and bottom surface of the cavity were not considered. In addition, particle-to-particle interactions were excluded because the particle flux needs to be low to prevent particle from clogging in the cavity during centrifugal filling (the targeted mean particle distance is larger than 10-times the particle diameter). Furthermore, an air velocity equivalent to the local rotating disk velocity is assumed.

The particle trajectory is governed by Newton’s law of motion and reads:

$$m_p \cdot \ddot{r}_p = F_{\text{drag}} + F_{\text{centrifugal}} + F_{\text{coriolis}},$$  

with $m_p$ the particle mass and $a_p$ the acceleration. The three acting forces are the viscous drag force $F_{\text{drag}}$ and two fictitious forces: the centrifugal force $F_{\text{centrifugal}}$ and the Coriolis force $F_{\text{coriolis}}$ (shown as vectors in Fig. 6).

The **drag force** acting on the particle with a diameter of $d_p$ results from the velocity difference between a particle and the rotating air (equivalent to the disk) $v_r$, the air density $\rho_g$ and the drag coefficient $C_d$:

$$F_{\text{drag}} = \frac{1}{8} \rho_g v_r^2 C_d \pi d_p^2.$$  

It is anti-parallel to the particle velocity $v_r$. The drag coefficient can be derived through analytical correlations provided by Schiller and Naumann [18] for laminar flow (Reynolds numbers, Re < 1000) around spherical particles:

$$C_d = \frac{24}{Re} \left(1 + 0.15 Re^{0.687}\right),$$

with $Re = \frac{\nu d_p}{\nu}$ and the kinematic viscosity $\nu$ of air.

The radial **centrifugal force** is defined through

$$F_{\text{centrifugal}} = -m_p \Omega \times (\Omega \times \dot{r}),$$

with the particle position radius $r$ (location relative to the disk center) and the disk angular velocity $\Omega$.

The **Coriolis force** reads

$$F_{\text{coriolis}} = -2m_p \Omega \times \dot{v}_r$$

and is normal to the particle velocity.

The resulting trajectory and velocity of an alumina particle with a diameter of 26 µm at a disk angular velocity of 1500 rotations per minute (rpm) are depicted in Fig. 6 and labeled as T1. The particle is injected with an offset radius $R_{\text{start}}$ of 2.4 mm and finally collides with one of the four disk-integrated stopper features at an incident radius $R_{\text{incident}}$ and velocity $v_{\text{incident}}$ of 21.6 mm and 2.2 m/s, respectively. A total flight time $t_{\text{flight}}$ of 112 ms was predicted (Table 1, T1). In addition, the trajectories of 1000 equal particles with the same process conditions were calculated with a uniform (green) and a 1/R² (red) feed distribution imposed on the central feed with a radius $R_{\text{max}}$ of 5 mm (Fig. 6, inset: feed distribution). The syringe particle feed process might be better represent by the hyperbolic than the uniform distribution. However, the predicted resulting incident distribution for both cases is close to equal and therefore indicates a robust process with a low sensitivity on the feed condition (Fig. 6, inset: incident distribution). Both graphs decay close to linearly with increasing radius and might indicate a nonuniform particle accumulation along the stopper (the noise of the curves is due to the limited number of calculated trajectories). The outer bound of all the trajectories is indicated by a dashed blue line and hits the stopper at a radius $R_{\text{incident max}}$ of 39.8 mm. It also depends on the stopper radius $R_s$, which in this case was 20 mm. The modeled trajectories and the incident distribution give an indication for the placement of the modules and the design of the cover-plate guiding structures.

Further trajectories for a smaller particle with a diameter of 22 µm (T2, Fig. 6, green trajectory) and an increased angular velocity of 2000 rpm (T3) were computed in a sensitivity analysis (Table 1). A significant change in incident radius from 21.6 mm to 36.2 mm was observed when reducing the particle diameter from 26 µm to 22 µm. This finding is important in the case of a polydisperse filler particle feed: A nonuniform particle bed might result, with the larger particles close to the disk center. However, the trajectory does not depend on the angular velocity of the disk (T3 is
congruent with T1, as indicated by the incident radius). The incident velocity increases for both parameter variations (T2 and T3).

Figure 6: Modeled particle trajectories in the disk reference system. The disk contains four stoppers at a distance \( R_s \) and a central feed hole with a radius \( R_{\text{max}} \) of 5 mm in the disk center. The three forces acting on the particle and the resulting relative velocity are depicted by red and green arrows, respectively. Two resulting trajectories (T1 rainbow colored, corresponding to the relative particle velocity scale; T2 green) according to parameters depicted in Table 1 and with a starting position of \( R_{\text{start}} \) are shown. The incident distribution of 1000 particles is indicated for the T1 conditions for two feed distributions (green and red line in the insets). The outer bound of the 1000 trajectories is extracted and indicated by the dotted blue line.

Table 1: Test case parameters (shaded ) and resulting characteristics of three different trajectories.

<table>
<thead>
<tr>
<th>Trajectories</th>
<th>T1</th>
<th>T2</th>
<th>T3</th>
</tr>
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<tbody>
<tr>
<td>( d_p ) [( \mu m )]</td>
<td>26</td>
<td>22</td>
<td>26</td>
</tr>
<tr>
<td>RPM [1/min]</td>
<td>1500</td>
<td>1500</td>
<td>2000</td>
</tr>
<tr>
<td>( R_{\text{incident}} ) [mm]</td>
<td>21.6</td>
<td>36.2</td>
<td>21.5</td>
</tr>
<tr>
<td>( R_{\text{incident max}} ) [mm]</td>
<td>39.8</td>
<td>42.4</td>
<td>39.6</td>
</tr>
<tr>
<td>( v_{\text{incident}} ) [m/s]</td>
<td>2.2</td>
<td>3.2</td>
<td>2.9</td>
</tr>
<tr>
<td>( t_{\text{flight}} ) [ms]</td>
<td>112</td>
<td>118</td>
<td>84</td>
</tr>
</tbody>
</table>

The filling front (dotted lines) of the evolving particle bed was experimentally investigated for two guiding-structure designs and module placements (Fig. 7). Polysilicate silica powder was injected through the central feed hole at 1500 rpm. The cross-shaped disk (Fig. 7a) with the radial placement of the module does not reflect the particle trajectories and hence results in a tilted fill front with respect to the chip area. On the spiral-shaped disk (Fig. 7b), the module is tilted and trajectory-like guiding structures are implemented, resulting in a more efficient fill front, which is close to parallel to the chip edge.

The fill fraction of particles in confined space, with a cavity height of 60 \( \mu m \) (typical for FCBOB packages), was demonstrated without the presence of solder balls, but with a glass cover plate (specimen as depicted in Fig. 11). Defect-free percolating particle beds were assembled using monodispersed silica spheres or faceted diamond powder with a size range of 10 to 53 \( \mu m \) (Fig. 8, a-d). The indicated fill fractions of 46 to 66 vol-% are close to the theoretical limit of dense packing in confined space as discussed in Goicochea et al. [19, 20]. Zones with dense packing can be recognized, especially for the 53-\( \mu m \) silica spheres (Fig. 8a).

Figure 7: Experimental evolution of the fill front (dotted line) for two different centrifugal disk designs: (a) cross-shaped disk and (b) spiral-shaped disk, with the intention to fill the chip area (dark gray) efficiently.

Figure 8: Cavities (60 \( \mu m \) high, no solder balls) filled with monodispersed silica spheres of 53 and 10 \( \mu m \) diameter and faceted diamond powder with a size distribution of 30 to 40 \( \mu m \). (a) to (c) Microscopic views through the cavities top glass. (d) Scanning electron micrograph (SEM) of a cross section through the cavity shown in (c).
The defect-free filling of 35-µm-high cavities populated with typical solder ball patterns with a minimum critical distance of 56 µm with spherical silica particles of 20 µm to 27 µm in diameter is depicted in Fig. 9, panels S1 to S3. Particle clogging can occur in zones of dense solder ball population (Fig. 9, panel S4). Dispensed particle clusters might be the origin. In addition, some locations exhibit shadowing defects, which might result from high particle fluxes or disk angular velocities. Both defects need further investigations to improve the process yield.

![Figure 9: Sequence of microscopic views through the top glass of cavities (35-µm high) populated with typical solder ball patterns (S1 to S3). They were filled with silica spheres with a diameter distribution of 20 µm to 27 µm. S4 illustrates two defect types observed: clogging and shadowing.](image)

**NECK FORMATION BY THE SELF-ASSEMBLY OF NANO PARTICLES BY CAPILLARY BRIDGING**

The formation of necks by capillary bridging can easily be achieved by the following experiment: A drop of a silver nanosuspension (e.g., 10-nm-diameter Ag nanoparticles dispersed in xylene as available from UT Dots) is dispensed onto a particle bed of monodispersed silica spheres, as shown in Fig. 10a. The evaporation of the solvent of the nanosuspension (e.g., at 60°C for xylene) results in the formation and evolution of capillary bridges. Fragile silver necks remain from the self-assembly of nanoparticles as soon as all liquid has been removed. An annealing step at 150°C for 30 min provides the necessary mechanical integrity for the silver necks for further processing and inspection (Fig. 10b) [21]. The silver concentration in the nanosuspension has a strong influence on the neck topology: Funicular and pendular necks result for silver concentrations of 0.57 vol-% and 0.16 vol-%, respectively (Fig. 10c,d). The pendular topology with its open pores is preferred as it allows complete evaporation of the solvent as well as backfilling of the adhesive matrix without voids (more details on the topologies can be found in [16]).

![Figure 10: (a) Sketch of a simple experiment to achieve necks by the evaporation of the solvent of the nanosuspension. (b) SEM image of the silver necks after annealing. (c) and (d) Micrographs of two distinct neck topologies resulting from 0.57 vol-% and 0.16 vol-% silver content in the nanosuspension: (c) funicular and (d) pendular.](image)

The uniform and robust formation of necks between filler particles in cavities needs to be investigated to render necking relevant for thermal underfill applications. For this purpose silicon cavities with a height of 60 µm, a footprint of 11 by 11 mm² and a glass cover were fabricated (Fig. 11). Use of an internal filter composed of pillars arranged in a row, separated by a spacing smaller than the filler particle diameter, results in a well-defined particle bed from the centrifugal filling of the cavity. The injection of the nanosuspension to achieve the necks and the final backfilling of the adhesive matrix are done through the available port.

![Figure 11: (a) Cross section and (b) top view of the silicon cavity test section for neck-formation investigations. The solvent of the nanosuspension can leave the cavity through the cavity in- and outlet during the evaporation step. The blue, red and green marks indicate observation locations.](image)

The silicon cavities were filled by centrifugation with monodisperse silica spheres with a diameter of 53 µm. They assemble in two layers: one close to the glass and one close to the silicon surface (Fig. 11, left panel: dark and light blue particle layer). Water was injected into the particle-filled cavity to trace the evolution of the liquid meniscus during the subsequent water-evaporation process with the optical microscope (Fig. 12a-f). The vapor exits through the in- and outlet port of the specimen (Fig. 11b).

At a temperature of 60°C, which is below the boiling point of water at atmospheric pressure, two distinct evaporation patterns can be observed in sequence:

**1. Dendritic network growth:** The formation of funicular capillary bridges by the growth of a dendritic network from...
the in- and outlet of the specimen can be observed (Fig. 12 a, c). The dendrite evolution follows defects in the particle bed, allowing for large meniscus curvatures.

2. Collapse of capillary bridges: A transition from the connected funicular to singulated pendular capillary bridges results from the evaporation of the liquid connections. Finally, the evaporation of the isolated water necks and collars occurs and can be observed as a moving front from the specimen in- and outlet (Fig. 12 b, d).

The dendrite growth and the collapse of capillary bridges at 100°C, the boiling point of water, occur uniformly across the particle bed (Fig. 12 e, f) and do not start from the specimen in- and outlet, in contrast to the water evaporation at 60°C. Hence, a higher neck uniformity can be expected. Furthermore, the total time for evaporation is reduced from 800 s to 60 s.

Evaporation pattern sequence

1) Dendritic Network Growth
2) Collapse of Capillary Bridges

Evaporation at 60°C

Evaporation at 100°C

To investigate the neck and collar uniformity within the specimen cavity, water was substituted by an aqueous nanosuspension filled with monodisperse polystyrene (PS) beads. A PS bead diameter of 100 nm and a particle loading of 1.25 vol-% were chosen for the investigation. The cavity cover plate and the filler particles were mechanically removed after the formation of the PS necks so that the number of collars formed on the cavity surface could be inspected by SEM (Fig. 13a). The local collar diameter and the collar yield can be derived. The latter is defined as the ratio of collar density on the surface to the filler particle density in close proximity to that surface (dark or light blue particle layer as presented in Fig. 11a for the top or bottom surface, respectively). The resulting collar yield at the inlet, the center and the outlet position in the cavity are reproduced in Fig. 14 for the bottom surface (silicon surface). The evaporation took place on a hot plate at three different evaporation temperatures (25°C, 60°C and 100°C). The collar topology formed below the boiling point of water resulted in the expected concave collar shape, including some radial cracks probably induced in the final drying step of the self-assembly process (Fig. 13b). At an evaporation temperature of 100°C only a collar ring remains, with a substantially smaller contact area to the spherical particle (Fig. 13c). The reduced contact may affect the thermal transport negatively. In contrast, a bottom collar yield of better than 0.7 is achieved for evaporation at 100°C (Fig. 14) and exhibits a high uniformity within the cavity. For the evaporation at 25°C, no collars could be observed in the center of the cavity. The slow evolution of the capillary bridging process and its initiation from the periphery of the cavity (Fig. 12 a, b) seem to result in the migration of the PS nanoparticles towards the in- and outlet. At 60°C, the uniformity is restored again, which might indicate the significance of the evaporation dynamics for the particle migration.

Figure 13: SEM top views towards the bottom surface of a mechanically opened cavity showing the assembled PS collars. The silica filler particles with 53 µm diameter were removed prior to this inspection. The visible collars result from the capillary bridging of an aqueous nanosuspension (100 nm PS 1.25 vol-%) at 60°C (a,b) and 100°C (c).
Figure 14: Collar yield on the bottom silicon surface after evaporation of the aqueous nanosuspension (100 nm PS 1.25 vol-%). The evaporation process was performed on a hot plate at three different temperatures. The collar yield at three different positions in the cavity is indicated and is a measure for the collar formation uniformity.

Furthermore, the influence of gravity and of a temperature gradient normal to the cavity surface on the collar yield were explored by three different heating scenarios. Two specimens were heated from the silicon side by a hot plate, with silicon as a bottom or top plate of the cavity (Table 2, note that top and bottom are defined by the gravitation arrow). For the third specimen, the evaporation temperature of 60°C was controlled by an oven, with silicon forming the bottom plate. A strong asymmetric collar yield results from the hot-plate experiments. Collars exist only on the heated silicon side, irrespective of gravity. A close to symmetric collar yield is obtained in the experiment with uniform thermal exposure in the oven. The temperature-gradient-induced asymmetric necking could be caused by thermophoresis [22] or by an asymmetric evolution of the meniscus in the cavity and needs further investigation.

Table 2: Collar formation yield at the top and bottom plate for three different heating scenarios. Neck formation was performed at 60°C with an aqueous nanosuspension (100 nm PS 1.25 vol-%). The gravity vector indicated defines top and bottom surface of the cavity.

<table>
<thead>
<tr>
<th>Heating scenario</th>
<th>Top 0%</th>
<th>55%</th>
<th>80%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom 42%</td>
<td>0%</td>
<td>97%</td>
<td></td>
</tr>
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</table>

Moreover, also the sensitivity of the collar diameter and yield to the nanoparticle loading of the nanosuspension was investigated. For this, the PS bead concentration of the aqueous nanosuspension was varied from 0.125 vol-% to 1.25 vol-%. Evaporation was performed on a hot plate at 60°C, with the silicon plate at the bottom. The bottom collar diameter and yield increase almost linearly with the particle loading from 11 µm to 25 µm and from 14% to 54%, respectively (Fig. 15). A collar diameter close to 40% of the filler particle diameter of 53 µm results from a nanosuspension particle loading of 0.75 vol-%. The neck topology is still pendular rather than the funicular topology resulting from a smaller particle loading of the silver nanosuspension (0.57 vol-%) in the simple neck formation experiment presented in Fig. 10a. The reason for this difference is the excess of the nanosuspension on top of the particle bed in the simple experiment, which is not the case for the cavity experiment.

Figure 15: Size and yield of the assembled collars at the bottom silicon plate vs. nanoparticle concentration in the nanosuspension. The 60-µm-high cavity was filled with 53-µm silica spheres. The self-assembly was performed with an aqueous suspension (100-nm PS spheres) on a hot plate at an evaporation temperature of 60°C and with silicon as the bottom plate.

An annealing step was used in the case of silver necks to achieve mechanical integrity of the enhanced thermal interconnects formed. However, metallic nanoparticles can only be used for investigating the neck formation, as they would cause electrical shorting between solder balls if used for thermal underfill applications. Hence, a substitution of the metallic nanoparticle with thermally conductive dielectric nanoparticles, such as alumina, is necessary. The required sintering temperature for ceramic materials to form mechanically robust necks exceeds the available thermal budget, which is defined by the liquidus temperature of the solder balls. Therefore, a novel reinforcement strategy is proposed. Bi-modal necks consisting of thermoplast and thermally conductive ceramic nanoparticles will be assembled. A subsequent annealing step above the softening temperature of the thermoplast will result in a wetting of the contact surfaces and the required adhesive bonds after the cool down to room temperature. In this way, two basic bi-modal necks can be formed:

**Interstitial necks:** The thermoplast and ceramic nanoparticles will be assembled simultaneously in a single capillary bridging event. The thermoplast nanoparticles are supposed to occupy interstitial positions uniformly in the hexagonal close packing (HCP) lattice of the densely packed ceramic nanoparticles (Fig. 16a).

**Core-shell necks:** Two sequential capillary-bridging process steps will be performed: the first to assemble the ceramic core and the second to add the thermoplast shell (Fig. 16b).
The formation of interstitial necks requires a stable dispersion of two material types in one carrier fluid. An aqueous PS and alumina nanosuspension was performed in this study. The assembly of the PS particles at interstitial positions is achieved by proper selection of their diameter and loading according to the available space and the number of interstitial positions with respect to the alumina particles. Octahedral and tetrahedral interstitials exist in the HCP lattice as shown in Table 3 [23].

**Table 3:** Relative diameter and count of interstitial types in a dense HCP lattice with respect to a single lattice particle

<table>
<thead>
<tr>
<th>Interstitial type</th>
<th>Relative diameter</th>
<th>Relative count</th>
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<tbody>
<tr>
<td>Octahedral</td>
<td>0.414</td>
<td>1</td>
</tr>
<tr>
<td>Tetrahedral</td>
<td>0.225</td>
<td>0.5</td>
</tr>
</tbody>
</table>

As compromise, PS particles with a diameter of 100 nm at a particle count ratio of 1.5 were selected for the use with alumina particles with 300 nm diameter. The achieved bi-modal assembly of interstitial necks using simultaneous neck formation is illustrated in Fig. 16c. The PS nanoparticles occupy interstitial positions with a high yield.

The sequential formation of core-shell necks allows an independent formulation of two different nanosuspensions without defined particle-diameter ratio. One limitation might be the surface tension and viscosity of the second nanosuspension so that the still fragile ceramic necks achieved in the first assembly step are not destroyed. Figure 16d shows a core-shell collar that consists of 300-nm alumina and 100-nm PS nanoparticles, both from an aqueous nanosuspension. Evaporation temperatures of 60°C and 100°C were chosen for the first and second assembly step, respectively, to achieve the targeted topology and uniformity (Fig. 13 b, c).

**Figure 16:** Bi-modal necks to achieve mechanically stable dielectric areal interconnects. Two possible topologies, the interstitial neck (a, c) and the core-shell neck (b, d) are shown. (a, b) Schematics of the simultaneous and the sequential process. Red and brown particles indicate the thermally conductive ceramic and the thermoplast material, respectively. The core-shell neck is formed by two subsequent capillary bridging processes of two different nanosuspensions. The resulting necks are shown in the SEM images below (c, d).

**Figure 17:** Core-shell necks and collars of 100-nm PS and 300-nm alumina nanoparticles after the annealing step at 140°C for 15 min. (a) The PS shell forms a continuous and smooth layer around the core structure. (b) A percolation path between the top and bottom surface of the cavity with enhanced thermal interconnects is formed by two collars and one neck.

**THERMAL RESPONSE**

Thermal test cavities with a silicon instead of the glass cover plate (equivalent to Fig. 11) are fabricated to perform the thermal characterization of the novel enhanced percolating thermal underfill. The silicon frame of the filled cavities is removed by dicing to provide sample composed of three layers (silicon – underfill – silicon) with a 10×10 mm² footprint. The specimens are mounted into a thermal tester, between two copper pistons and exposed to a 1D heat flux. The measured temperature difference between the two ends of the copper piston and the thickness of the three layers of the specimens allows the extraction of the effective thermal conductivity of the enhanced thermal underfill (for details on the thermal characterization method, see [6, 19]).

Benchmarking of the enhanced percolating thermal underfill bondlines with filler particles only and with filler particles with necks was performed against silica or alumina loaded capillary underfills with an effective thermal conductivity below 1 W/m-K (Fig. 18). Percolating filler particles assembled by centrifugation result in an improvement beyond the 2 W/m-K mark. Effective thermal conductivities of more than 3 W/m-K were achieved with diamond filler particles and silver necks, demonstrating the superiority of the sequential underfill formation process. The use of the hierarchical self-assembly of micro- and nanoparticles results in a fivefold improvement over state-of-the-art solutions.
CONCLUSIONS

The sequential thermal underfill process with the hierarchical self-assembly of micro- and nanoparticles achieves a close to fivefold superior thermal performance (up to 3.8 W/m-K) as compared to capillary underfills. The centrifugal filling of the micron-sized filler particles results in a percolating particle bed in the solder ball cavity. An enhanced thermal contact is achieved by the formation of thermal necks resulting from nanoparticle self-assembly by capillary bridging. To reduce process complexity, the percolating thermal underfill could be deployed first without the necks, which already yields effective thermal conductivities of more than 2 W/m-K. The following characteristics were identified for the self-assembly steps:

1) Centrifugation of filler particles:
   - 2D numerical modeling can be used to predict the particle trajectories and their distribution, supporting the design of guiding structures and the placement of the modules on the centrifugal disk.
   - Spiral-like guiding structures that follow particle trajectories result in an efficient filling of cavities.
   - A strong dependency on the particle size was observed for the particle trajectories. Therefore, nonuniform particle beds might result from polydisperse particle assemblies (needs to be validated).
   - Defect-free particle fill fractions of 46 vol-% to 66 vol-%, i.e., close to the theoretical limit in a confined space and above the percolation threshold, could be achieved.
   - Percolation could be achieved for spherical and faceted particles, expanding the available material choices.
   - Defect-free particle bed formation in solder ball arrays was presented. However, clogging and shadowing defects were also identified in the densest solder ball populations. Hence, further investigations are needed to improve the robustness of the process.

2) Neck formation by capillary bridging of nanoparticles:
   - The capillary-bridging process is governed by two distinct evaporation patterns that occur in sequence: 1) dendritic network growth and 2) the collapse of capillary bridges. They occur uniformly or are initiated from the cavity periphery, depending on the evaporation temperature above or below the boiling point of the nanosuspension.
   - Uniform neck formation in the cavity plane could be achieved at temperatures above 60°C for aqueous nanosuspensions. The reason for nanoparticle migration at lower temperatures needs still further investigation.
   - The evaporation process needs to be performed in an oven to prevent thermal gradients normal to the cavity surface, which would result in asymmetric neck formation at the top and bottom surface. The origin of the asymmetric neck formation on a hot plate needs further investigation.
   - Nanosuspensions with a nanoparticle loading of 0.75 vol-% seem to be sufficient, as they result in relative neck diameters of 40% of the filler particle diameter.
   - The assembly of bi-modal necks (ceramic and thermoplastic nanoparticles) allows the mechanical reinforcement of the achieved dielectric necks by an annealing procedure at temperatures below the liquid temperature of the solder balls. Two topologies were presented:
     - Interstitial necks: PS particles are uniformly assembled at interstitial positions between the alumina particles. Hence, the nanosuspension needs to be suitable to host both particles. However, only one capillary bridging step is needed. A 3:1 diameter and a 1:1.5 particle count ratio were selected and resulted in the desired assembly.
     - Core-shell necks: PS particles are assembled around the alumina neck. Hence, two capillary bridging processes are needed. The alumina particles were assembled at 60°C, and followed by an assembly step at 100°C for the PS shell.
   In both cases, an annealing step performed at 140°C resulted in mechanically reinforced necks.

FUTURE WORK

In a next study, the mechanical properties of the percolating thermal underfill need to be investigated with respect to the neck diameter and topology. In addition, reliability testing has to be performed to identify characteristic failure modes of the novel composite material.

Other opportunities for the self-assembly of nanoparticles by capillary bridging is the formation of electrical joints at low temperatures of less than 200°C with silver or copper nanoparticles. A first experiment was performed by injecting a silver nanosuspension between two silicon dies, one of them populated with copper pillars (Fig. 19). The resulting electrical necks might reduce the thermo-mechanical stress in the package and might allow higher current densities due to a better electromigration stability of the necks compared to solder. A main challenge will be to prevent electrical shorting.
between pillars, which could be achieved by precise deposition of the metallic nanoparticles without percolation between two pads.

Figure 19: SEM image of two silver necks formed by capillary bridging between copper pillars and a pad. The annealing of the silver neck was performed at 150°C.

NOMENCLATURE

- \( a_p \) acceleration of filler particle \([m/s^2]\)
- \( C_d \) drag coefficient [-]
- \( d_p \) filler-particle diameter \([m]\)
- \( F_{centrifugal} \) centrifugal force \([N]\)
- \( F_{coriolis} \) Coriolis force \([N]\)
- \( F_{drag} \) drag force \([N]\)
- \( m_p \) mass of filler particle \([kg]\)
- \( R \) filler-particle feed position \([m]\)
- \( Re \) Reynolds number [-]
- \( R_{incident} \) filler-particle incident position \([m]\)
- \( R_{max} \) central feed radius \([m]\)
- \( rpm \) revolutions per minute \([1/min]\)
- \( R_s \) stopper radius \([m]\)
- \( R_{start} \) specific filler-particle feed position \([m]\)
- \( t_{flight} \) filler-particle flight time \([s]\)
- \( v_{incident} \) filler-particle incident velocity \([m/s]\)
- \( v_r \) relative filler-particle velocity \([m/s]\)
- \( \nu \) kinematic viscosity \([m^2/s]\)
- \( \Omega \) angular velocity \([rad/s]\)
- \( \rho_g \) gas density \([kg/m^3]\)

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