Probability of conductive bond formation in a percolating network of nanowires with fusible tips

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Meeting the heat dissipation demands of microelectronic devices requires development of polymeric composites with high thermal conductivity. This property is drastically improved by percolation networks of metallic filler particles that have their particle-to-particle contact resistances reduced through thermal or electromagnetic fusing. However, composites with fused metallic fillers are electrically conductive, which prevents their application within the chip-board and the inter-chip gaps. Here, we propose that electrically insulating composites for these purposes can be achieved by the application of fusible metallic coatings to the tips of nanowires with thermally conductive but electrically insulating cores. We derive analytical models that relate the ratio of the coated and total nanowire lengths to the fraction of fused, and thus conductive, bonds within percolating networks of these structures. We consider two types of materials for these fusible coatings. First, we consider silver-like coatings, which form only conductive bonds when contacting the silver-like coating of another nanowire. Second, we consider liquid metal-like coatings, which form conductive bonds regardless of whether they contact a coated or an uncoated segment of another nanowire. These models were validated using Monte Carlo simulations, which also revealed that electrical short-circuiting is highly unlikely until most of the wire is coated. Furthermore, we demonstrate that switching the tip coating from silver- to liquid metal-like materials can double the fraction of conductive bonds. Consequently, this work provides motivation to develop scalable methods for fabrication of the hybrid liquid-coated nanowires, whose dispersion in a polymer matrix is predicted to yield highly thermally conductive but electrically insulating composites. Published by AIP Publishing. https://doi.org/10.1063/1.5026578

The current industry-standard for computer chip integration with circuit boards is a “flip-chip” packaging technology that uses filled polymeric materials to facilitate thermal transport between components. These filled polymeric materials are used between the chip’s back-side and the heat spreader, between the heat spreader and heat sink,1,2 and between the chip’s front side and the circuit board. The gap between the chip and the circuit board is also bridged by solder micro-bump vias that send electrical signals between the chip and the circuit board. Consequently, filled polymers in this gap (also referred to as underfill materials) must be electrically insulating to prevent signal corruption.3

Filled polymers improve thermal transport by filling in micro-air gaps between two rough surfaces and thereby decrease the thermal contact resistance. Silicone or similar greases are typically used as the base material for underfills.4 To improve the inherently low thermal conductivity of these base materials (~0.2–0.4 W m⁻¹ K⁻¹), high thermal conductivity solid additives such as diamond, silver,5,6 aluminum nitride,7 graphite,8 boron nitride,3,9–11 and even liquid metals (LMs)12–14 are added. A large volume fraction of filler particles is typically used in these composites to achieve particle percolation and further improve thermal transport.15 Despite these efforts, the effective thermal conductivity of these composites usually remains below 2 W m⁻¹ K⁻¹. One of the dominant mechanisms limiting the effective thermal conductivity of these composites is the small interfacial contact area between filler particles, which leads to large particle-to-particle thermal contact resistances.5,15,16 Previous approaches such as thermal sintering17,18 and microwave welding5,6 of the filler particles have been shown to significantly reduce the particle-to-particle contact resistance. For example, Seshadri et al.5,6 found that this treatment increased the effective thermal conductivity of a polymer-Ag nanowire composite 40-fold. However, these processes also make the metal nanowire network electrically conductive, which restricts the applicability of the resulting composite. In addition, it would be challenging to utilize high thermal sintering and microwaving in integrated circuit packaging workflow.

In this work, we argue that the use of hybrid nanowires can produce highly thermally conductive composites that are also electrically insulating. The proposed nanowire core is a thermally conductive but electrically insulating material (e.g., diamond, undoped silicon, germanium, and aluminum oxide), whereas the nanowire tips are modified with a fusible metallic coating [see Fig. 1(a)]. The role of the fusible coating is to create thermally conductive bonds with other nanowires. We show that by introducing a break in the metallic coating (i.e., only coating the nanowire tips), the individual bonds between nanowires can be electrically conductive and still produce an overall electrically insulating composite.

In general, two categories of metallic materials that can form such fusible coatings exist. The first type of fusible coating consists of solid metal films that are fused through post-processing such as thermal sintering or electromagnetic energy exposure (e.g., “microwave-welding”). These are exemplified...
by silver coatings, which form conductive bonds (“good bonds”) when contacting the silver coated segment of another wire and subsequently microwave welded [see Fig. 1(b)]. However, these silver coatings will not form good bonds when in contact with an uncoated portion of another wire (for example, when in contact with the silicon core of a wire). The second type of fusible coating is exemplified by room temperature liquid metal (LM) films. These coatings form “good bonds” (i.e., thermally conductive) when in contact with coated and non-coated wire segments and do not require post-processing [see Fig. 1(c)]. While such hybrid nanowires are currently attractive side,21,22 and Janus colloidal particles, “matchsticks” with one attractive side,23–31 have been developed and studied from percolation perspectives. In addition, a variety of core-shell particles have been developed in order to improve thermal transport between the filler particles and the base material.32–41 Furthermore, Majidi and coworkers recently showed that iron oxide particles can be conformally coated with LM if a wetting layer (e.g., Ag) is utilized. When brought together through composite compression, the uniform LM coatings merged at the point of contact and created an enlarged and electrically conductive path.42 Consequently, from a material science point of view, fabrication of the proposed hybrid nanowires should be feasible. In this paper, we develop the theoretical framework that can be used to guide and motivate the development of these hybrid filler particles.

For identical randomly dispersed nanowires with aspect ratio $p > 30$, the volume fraction needed to achieve percolation, $\phi_c$, and the average number of bonds per object, $B_c$, at this threshold are equal to $C_{per}/p$ and $C_{per}$, respectively (with $C_{per} \approx 1.4–1.5$, see detailed discussion in the supplementary material).5,43,44 To achieve a high thermal conductivity composite, most of the bonds or intersections within the percolation network ($B_c$) need to be conductive (of the “good” type).

If nanowires with thermally conductive, but electrically insulating, cores are partially modified with the first type of fusible coatings, such as Ag, a “good bond” will only form during Ag-Ag contact [see Fig. 1(b)]. In turn, core-core contacts will have a small contact area that leads to a “bad bond” with large contact resistance. Similarly, “bad bonds” will also form during Ag-core contact. If we assume that the probability of contact formation is uniform along the length of the wire, the probability of forming a “good bond” ($P_{gb-Ag}$) between a partially coated wire and an uncoated wire is equal to ratio of the Ag-coated length to the total length, $L_{Ag}/L_T$. For two identically modified nanowires, the probability of making a good bond can be calculated through the length-weighted summation of probabilities of forming a good bond in the coated and uncoated segments. Since the probability of forming a good bond in the coated segment is equal to $L_{Ag}/L_T$ and the probability of forming a good bond in the uncoated segment is zero, the overall probability of forming a good bond for Ag-modified wires is

$$P_{gb-Ag} = \left(\frac{L_{Ag}}{L_T}\right) \left(\frac{L_{Ag}}{L_T}\right) + \left(1 - \frac{L_{Ag}}{L_T}\right) 0 = \left(\frac{L_{Ag}}{L_T}\right)^2.$$  \hspace{1cm} (1)

In the case where the hybrid nanowires are partially modified with a liquid metal (and the threshold forces required for breaking the LM oxide occur),45–48 a good bond will form during LM-LM and LM-core contact [see Fig. 1(c)]. Using the same assumptions as in the Ag-case above, the probability of forming a good bond ($P_{gb-LM}$) between a partially coated wire and an uncoated wire is equal to the ratio of the LM-coated length to the total length, $L_{LM}/L_T$ [see Fig. 1(c)]. For two identically modified nanowires, the probability of making a good contact can be calculated through the length-weighted summation of probabilities of forming a good contact in the coated and uncoated segments. Since the LM-coated length always forms good contacts, the probability of forming a good contact in the coated segment is equal to 1. The probability of forming a good contact with the uncoated segment is dictated by the second object and is equal to $L_{LM}/L_T$. Thus, the overall probability of forming a good bond for LM-modified wires is

$$P_{gb-LM} = \left(1\right) \left(\frac{L_{LM}}{L_T}\right) + \left(1 - \frac{L_{LM}}{L_T}\right) \frac{L_{LM}}{L_T} = 2 \frac{L_{LM}}{L_T} \left(\frac{L_{LM}}{L_T}\right)^2.$$  \hspace{1cm} (2)

The quadratic nature of the dependence of $P_{gb-Ag}$ and $P_{gb-LM}$ on $L_{LM}/L_T$ is notable. In the case of $P_{gb-Ag}$, this relationship is unfavorable because for small Ag modification of
the nanowire tips, the probability of having predominantly good bonds is small (e.g., \( P_{gb-\text{Ag}} \approx 0.45 \) for nanowires with three equal-sized segments, \( L_{\text{Ag}}/L_T = 0.67 \)). In turn, the concave down quadratic nature of Eq. (2) is highly beneficial because even a small LM modification of the nanowire tips leads to a large probability of having predominantly good bonds (e.g., \( P_{gb-\text{LM}} \approx 0.9 \) for nanowires with three equal-sized segments, \( L_{\text{LM}}/L_T = 0.67 \)).

For an electrically insulating nanowire with LM- or Ag-coated tips, electrical short circuits can occur in the two modes illustrated in Fig. 1(d). Specifically, these modes consist of (i) a chain of contacts between the metal-coated tips or (ii) electrical-bridging of a nanowire’s uncoated segment by the metal-coated tip(s) of other wires. The first scenario is highly unlikely because it involves contact between three or more wires at a single nanowire segment. Specifically, the probability of a single such three wire contact scales with \( (L_{x}/2L_T)^3 \), while that of an entire chain with \( N \) wires with \( (L_{x}/2L_T)^N \), where the subscript \( x \) corresponds to either an Ag or LM coating. Consequently, the probability of short circuit in this mode rapidly decays to zero even for a chain of a few wires (e.g., for 5 wires and even high \( L_x/L_T = 0.9 \), \( (L_{x}/2L_T)^5 \approx 10^{-6} \)). Analytical estimation of the probability of electrical short circuit in the second scenario is more difficult. However, in a two-particle interaction, it cannot occur until the length of the coated tip is greater than that of the gap, i.e., \( L_{x}/2 > L_T - L_x \). Here, we assume that three- or more particle interactions in this mode are highly unlikely (where bridging of the gap would occur by a series connection of tips of multiple other wires). In other words, electrical short circuit has zero probability of occurring if the length of an individual tip coating is shorter than one third of the total length \( (L_{x}/2 < L_T/3) \). If \( L_{x}/2 > L_T/3 \), there is a finite, but small, probability of an electrical short circuit that could involve a mix of the modes illustrated in Fig. 1(d).

In order to validate our analytical expressions relating the individual wire geometry to the probability of forming conductive bonds with the wire network, we developed a two-dimensional Monte Carlo simulation. The baseline code for generation of randomly dispersed and oriented “stick” populations (i.e., wires with zero width) and detection of percolation paths in this network is based on the recent work of Ackermann et al.\(^4\) In this approach, the generated population of wires with a specified initial length is plotted in a binary image, which also has horizontal lines across the top and bottom. Subsequently, the length of the wires is increased until percolation (i.e., bridging of top and bottom lines via a wire chain) is detected through image processing in Wolfram Mathematica. In order to calculate the number of wire intersections (i.e., assumed bonds) in each image, we have modified the Ackermann et al.\(^4\) code to plot semi-transparent wires. The points of the intersection of such semi-transparent wires are darker than the wires and are thus easily isolated and detected through selective image color thresholding. Our simulation results for uniform wires compare well against the benchmark analytical formula for a critical number of wires and bonds per wire \( (B_c \approx 1.4–1.5) \) required to achieve percolation developed by Balberg et al.\(^4\) (see supplementary material).

To count the number of “good” and “bad” bonds within a network of percolating wires with modified tips, we first generated a population of \( N \) homogenous wires and used the baseline algorithms to reveal the length required to achieve percolation and the total number of wire intersections per \( N \) [\( B_t \) illustrated in Fig. 2(a)]. Subsequently, each wire was divided into three segments consisting of outer coated tip segments and a bare center segment corresponding to the \( L_x/L_T \) of interest [see example in Fig. 2(b)]. Based on this population of heterogeneous wires, two separate images with just inner segments and just outer tips were generated. For
the Ag-modified wires, the number of good bonds per \( N \) (\( B_{gb} \)) was calculated by counting the number of wire intersections in the latter images that just contained the tips (i.e., in this case, Ag-Ag bonds). In turn, for the LM-modified wires, the number of good bonds per \( N \) was calculated by counting the number of bad bonds per \( N \) [\( B_{gb} \): core-core bonds highlighted in Fig. 2(c)] within the core-only image. Subsequently, the number of good bonds and probability of forming a good bond were calculated as \( B_{gb} = B_t - B_{gb} \) and \( P_{gb} = B_{gb}/B_t \). In addition, the image that only contained the tips was used to check if electrical percolation has occurred [see Fig. 2(d)]. In all of these cases, the algorithms for intersection counting and percolation detection described above were utilized.

The results presented in Figs. 2(e) and 2(f) are an average of 500 generated wire populations for each \( N \) in the range of \( N = 25 \) to \( N = 155 \). We iteratively determined that simulating 500 images per given condition was sufficient (i.e., results were not improved much by increasing the number of images). For each of these wire populations, calculations were performed with \( L_t/L_T \) in the range of 0.05–0.97 (the image processing algorithms faced resolution limits for \( L_t/L_T > 0.97 \)). The probability of forming an electrical percolation, \( P_{gb} \), was determined as the number of electrical percolations that occurred divided by the total number of simulated populations per given setting (i.e., 500).

The plot in Fig. 2(e) demonstrates that, in agreement with our reasoning, the probability of forming good bonds is nearly independent of the number of wires within the population (variation of \( \pm 5\% \) in simulation results). This enables us to present the simulation results, averaged over all simulated \( N \) (i.e., 7000 simulated wire populations), directly in terms of \( P_{gb} \) variation with \( L_t/L_T \). The plot in Fig. 2(f) demonstrates excellent agreement between simulated \( P_{gb-Ag} \) and that predicted using Eq. (1), as well as simulated \( P_{gb-LM} \), and that predicted using Eq. (2). Furthermore, \( P_{gb} = 0 \) up to the \( L_{LM}/L_T = 0.67 \) limit discussed above. Moreover, \( P_{gb} \) remains far below 1% until \( L_{LM}/L_T = 0.9 \), i.e., wires that are coated mostly with the metal and have only a short uncoated segment in the center. As expected, when the gap in the metallic coating nearly vanishes, \( P_{gb} \) increases rapidly, reaching 30% at \( L_{LM}/L_T = 0.97 \) (and 1 once the wires are fully coated).

Thus far, we have discussed ideal heterogeneous nanowire population consisting of identical particles. However, all realistic fabrication schemes will result in some variability in the length of the fusible coating, which can have impact on the probabilities of forming good bonds and of the occurrence of electrical short circuits. If we assume that the variability in \( L_t/L_T \) is random in nature, we can characterize it by a truncated Gaussian distribution with standard deviation \( \sigma_{L_t/L_T} \). The upper bound of this probability distribution corresponds to cases where the coated tips merge, resulting in a fully coated wire (i.e., when \( L_t/L_T = 1 \) and \( \sigma_{L_t/L_T} = 0 \)). From Eq. (1), we can derive expression for the standard deviation of \( P_{gb-Ag} \) as

\[
\sigma_{P_{gb-Ag}} = \sigma_{L_t/L_T} \left( \frac{dP_{gb-Ag}}{d(L_{Ag}/L_T)} \right) = 2\sigma_{L_t/L_T} \left( \frac{L_{Ag}}{L_T} \right). \tag{3}
\]

In turn, from Eq. (2), we can derive expression for the standard deviation of \( P_{gb-LM} \) as

\[
\sigma_{P_{gb-LM}} = \sigma_{L_{LM}/L_T} \left( \frac{dP_{gb-LM}}{d(L_{LM}/L_T)} \right) = 2\sigma_{L_{LM}/L_T} \left( 1 - \frac{L_{LM}}{L_T} \right). \tag{4}
\]

Due to the concave and convex nature of the quadratic equations (1) and (2), the trends for \( \sigma_{P_{gb-Ag}} \) and \( \sigma_{P_{gb-LM}} \) with \( L_t/L_T \) are opposite. For Ag modified wires, an increase in the coating length increases \( \sigma_{P_{gb-Ag}} \). This trend can result in a moderately high level of uncertainty, for example, for \( L_{Ag}/L_T = 0.66 \pm 0.2 \) (95% confidence interval with assumed truncated Gaussian distribution with standard deviation \( \sigma_{L_{Ag}/L_T} = 0.1 \)), \( \sigma_{P_{gb-Ag}} = 0.13 \) and \( P_{gb-Ag} = 0.44 \pm 0.26 \) (95% confidence interval). In contrast, for LM modified wires, an increase in the coating length decreases \( \sigma_{P_{gb-LM}} \). Thus, with the same wire geometry with \( L_{LM}/L_T = 0.66 \pm 0.2 \) (95% confidence interval with assumed truncated Gaussian distribution with standard deviation \( \sigma_{L_{LM}/L_T} = 0.1 \)), \( \sigma_{P_{gb-LM}} = 0.07 \) and \( P_{gb-LM} = 0.89 \pm 0.14 \) (95% confidence interval). These values are moderate, implying that in the case of the LM modified wires, the probability of forming thermally conductive bonds is not significantly affected by the wire-to-wire variations. It is important to note that both \( \sigma_{P_{gb-Ag}} \) and \( \sigma_{P_{gb-LM}} \) are zero when \( L_t/L_T = 1 \) because \( \sigma_{L_t/L_T} = 0 \) (the truncated Gaussian distribution bound).

Quantifying the increase in probability of forming an electrical path and hence electrical conduction across the composite due to variability in \( L_t/L_T \) resulting from fabrication imperfections (i.e., \( \sigma_{L_t/L_T} > 0 \)) analytically is more challenging. \( P_{gb} \) could increase significantly if wires with higher values of \( L_t/L_T \) have a variable gap width (with even some possibility of closing the gap). In order to quantify this possibility, we simulated populations of nanowires with a large range of \( \sigma_{L_t/L_T} \) of 0.1–0.3. The results presented in the plot in Fig. 3 show that \( P_{gb} \) increases faster at lower \( L_t/L_T \) when \( \sigma_{L_t/L_T} \) increases. However, even for a very large uncertainty in the wire modification length of \( \sigma_{L_t/L_T} = 0.3 \), \( P_{gb} \) remains below 0.001 and 0.01 for \( L_t/L_T \) of 0.76 and 0.88, respectively. Consequently, even with a large variability in the
nanowire geometry, electrical short-circuiting of the material is highly unlikely. We note that this trend is independent of whether the wire tips are coated with Ag-like or LM-like materials.

The unique heterogeneous nanowire structure proposed in this letter offers a promising solution path to increasing thermal conductivity of the polymer composites, with negligible risk of electrical short-circuiting. The latter characteristic is achieved despite the application of metallic fusible coatings on the nanowires and is enabled through an introduction of a break in the coatings. Specifically, electrical percolation was shown to be nearly impossible for $L_x/L_T < 0.67$ and highly unlikely until $L_x/L_T$ approaches 1 (i.e., fully coated wire). These stipulations were confirmed through Monte Carlo simulations, which were also used to quantify the effect of wire-to-wire variability in the coating length. Even with a large variability in the coating length of $\sigma_{L_x/L_T} = 0.3$ (i.e., higher chance of electrical bridging non-coated wire segments), $P_{\text{ep}}$ remained below 0.1% and 1% for $L_x/L_T$ of 0.76 and 0.88, respectively.

Our work clearly demonstrates the advantage of utilizing liquid metal or silver type tip coatings. Specifically, as shown in Fig. 2(f), for $L_x/L_T = 0.67$ (i.e., equisized segments), $P_{gb-LM}$ is about 0.9, which is twice higher than $P_{gb-Ag}$ of only 0.45. Since for such wire geometry $P_{\text{ep}}$ is approximately zero, dispersion of the LM-modified nanowires in a polymer matrix should lead to formation of a highly thermally conductive composite that is electrically insulating. Since such materials are highly desired for integrated circuit underfills, this work provides motivation to develop scalable methods for fabrication of the hybrid LM-coated nanowire structures.

See supplementary material for Monte Carlo simulation benchmarking against classical percolation theory.

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