Chapter 8
Thermal Interface Materials in Electronic Packaging

Abstract With the continual increase in cooling demand for electronic packaging, there has been an increased focus within the microelectronics industry on developing high performance thermal solutions. Thermal interface materials (TIMs) play a key role in thermally connecting various components of the thermal solution. As electronic assemblies become more compact and there is an increase in processing bandwidth, escalating thermal energy has become more difficult to manage. The major limitation has been nonmetallic joining using poor TIMs. The interfacial, versus bulk, thermal conductivity of an adhesive is the major loss mechanism and normally accounts for an order magnitude loss in conductivity per equivalent thickness. The next generation TIM requires a sophisticated understanding of material and surface sciences, heat transport at submicron scales, and the manufacturing processes used in packaging of microelectronics and other target applications. Only when this relationship between bond line manufacturing processes, structure, and contact resistance is well understood on a fundamental level, will it be possible to enhance interfacial thermal conductance and advance the development of miniaturized microsystems. TIMs are widely needed to improve thermal contacts for facilitating heat transfer in electronic packaging, such as that associated with the flow of heat from a microprocessor to a heat spreader or a heat sink in a computer. A TIM is commonly in the form of paste, solder, or a resilient sheet that serves to fill a gap between the two adjoining surfaces. The resiliency helps the conformability. The performance of a TIM is enhanced by conformability of the interface material to the topography of the mating surfaces because the air residing in the valleys in the surface topography is thermally insulating and should be displaced by the interface material. This chapter will discuss interfacial conduct mechanism and review current status and future trends of commercial and advanced TIMs, including metallic, organic, graphite, hybrid, and nanotechnology-based TIMs.

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Thermal Joint Conductance and Selection of Thermal Interface Materials

Thermal management is meant to ensure a long-term lifetime and functioning of electronic components such as power semiconductors in electronic circuits. It all begins with a profound knowledge of the occurring power dissipation and of the whole thermal path. Any engineering surface of the electronic components is rough on a microscopic level due to the presence of microscopic asperities. When two such rough surfaces come into contact during assembly of electronic packaging, the actual contact occurs only at a few discrete spots, usually at the high points of the two mating surfaces. Typically, the ratio of real contact area to apparent contact area is approximately 1–2%. Heat flowing from one body into the other is constricted to flow through the actual contact spots because the thermal conductivity of the solid contact spots is much higher than that of the surrounding gap which is filled with air in most electronic applications. TIMs are often inserted between the surfaces of a contact pair to reduce the thermal contact resistance. Although they typically have lower thermal conductivity than the substrate, they are highly compliant and hence, under the application of relatively small contact pressure, deform to conform to the geometry of the adjacent rough surfaces. A part of the low thermal conductivity gas present is therefore replaced by a higher conductivity material. This leads to a decrease in the constriction of the heat flow lines, and an increase in the contact conductance (Singhal et al. 2004). The heat transfer of these complex joints is governed by contact pressure; number, size, and shape of contact spots and voids; types of fluid in voids; pressure of fluid in voids; hardness and flatness of contact surfaces; modules of elasticity of contact surfaces; surface cleanliness; and property of the TIM used in the joint.

Thermal Joint Conductance

The contact interface configuration can be divided into conforming rough surfaces, and nonconforming wavy, convex, or concave interfaces. At this point the thermal joint conductance will be derived based on the assumption of conforming surfaces in which the voids are so small, thermal energy is mainly transferred by conduction, not by convection. In fact, the assumption of the conforming rough surfaces is close to most cases of the electronic packaging contact interfaces. Because radiation heat transfer at most interfaces is negligible or nonexistent, it will not be included in this analysis. The thermal joint conductance, h_j, of the interface formed by two conforming, rough surfaces is the sum of contact conductance and gap conductance, which is given by (Yovanovich et al. 2004)

$$h_\mathrm{j} = h_\mathrm{c} + h_\mathrm{g} = 1.25 k_\mathrm{s} \frac{m}{\sigma} \left(\frac{P}{H} \right)^{0.95} + \frac{k_\mathrm{g}}{Y + \sigma M}, \tag{8.1}$$

where h_c is contact conductance, h_g is the gap conductance. k_s is the harmonic mean thermal conductivity of the interface, and can be obtained by $k_s = 2\,k_1 k_2/(k_1 + k_2)$, k_1 and k_2 are thermal conductivity of two joint solids, respectively. σ is the combined RMS (Root-Mean-Square) roughness and can be obtained by $\sigma = \sqrt{\sigma_1^2 + \sigma_2^2}$, σ_1 and σ_2 are the RMS roughness of two joint surfaces, respectively. m is the effective mean absolute asperity slope of the interface and can be obtained by $m = \sqrt{m_1^2 + m_2^2}$, m_1 and m_2 are the absolute asperity slope of two joint surfaces, respectively.

The surface asperity slope is frequently not given. For the joint interface between aluminum heat sink and ceramic packages, the mean absolute asperity slope can be approximated by the correlation equation (Yovanovich et al. 2004):

$$m = 0.125\ (\sigma \times 10^6)^{0.402}, \tag{8.2}$$

which was developed for the surface roughness range:

$$0.216\,\mu\text{m} \leqslant \sigma < 9.6\,\mu\text{m}, \tag{8.3}$$

P represents the contact pressure, and H_c is the surface microhardness of the softer of the two contacting solids. The microhardness is in general complex because it depends on several geometric and physical parameters, such as the Vickers microhardness correlation coefficients. For the relative contact pressure range:

$$10^{-5} < P/H_c < 2 \times 10^{-2}. \tag{8.4}$$

The gas parameter M accounts for rarefaction effects at high temperatures and low gas pressures. This gas-surface parameter depends on the thermal accommodation coefficients, the ratio of specific heats, the Prandtl number, and the molecular mean free path of the gas. This complex gas surface parameter depends on gas pressure and temperature according to the relationship. Its value is 0.081 for air at 1 atm and 100°C, 0 for liquids (Yovanovich et al. 2004).

Although this conforming rough surface model was developed for bare surfaces, it can also be applied to interfaces with thermal grease, assuming that the grease behaves as a liquid and fills all gaps between the contacting asperities and substituting $M = 0$ and the thermal conductivity of the grease into the gap conductance relationship in equation (8.1). However, when solid interstitial materials are used, such as thermal compounds, elastomers, or adhesive tapes, the joint conductance problem becomes much more complicated because the use of a solid interstitial material introduces an additional interface to the problem. Using thermal resistance concepts, the overall joint conductance for this problem is determined by the series combination:

$$1/h_j = 1/(h_{j,1}) + t/k + 1/(h_{j,2}), \tag{8.5}$$

where $h_{j,1}$ and $h_{j,2}$ refer to the joint conductance between each of the contacting surfaces and the interfacial material, and t and k are the average thickness and thermal conductivity of the interstitial layer. Completing this analysis requires characterization of the relevant surface parameters, such as the slope, roughness, and microhardness for the various interstitial materials. In addition, for elastomeric materials, the layer thickness t is not constant but instead depends on the contact pressure. Additional research is needed before a model can be developed to address this complex phenomenon.

For example, the aforementioned models will be used to calculate the joint resistances for the interface formed by an aluminum 6063-T5 heat sink and alumina (Al_2O_3) package. The thermal conductivities of the heat sink and ceramic package are $k_1 = 201$ W/m K and $k_2 = 20.9$ W/m K respectively. The harmonic mean thermal conductivity of the interface is $k_s = 37.85$ W/m K. Because the microhardness of the aluminum alloy is 1,094 MPa, which is much less than that of the alumina, it will be used to compute the contact parameters. Based on a surface roughness for fly cut aluminum of $\sigma_1 = 0.4$ μm and a surface roughness for ground alumina of $\sigma_2 = 1.3$ μm, the effective surface roughness of the interface is calculated as $\sigma = 1.36$ μm. The surface slopes are $m_1 = 0.139$, $m_2 = 0.0865$, respectively. The effective surface slope of the interface is therefore $m = 0.164$. Therefore, the join resistance of a typical aluminium-ceramic interface can be calculated for contact pressures between 0.007 and 0.35 MPa, which includes the practical microelectronic pressure range of 0.07 and 0.17 MPa. The greatest joint resistances are found when air is present in the interstitial gap. In the contact pressure range of 0.007–0.35 MPa, the air joint resistance goes from 2.665 to 1.903 cm^2 °C/W. When silicon grease is placed in the gap, the joint resistance is much smaller than the bare interface. The calculated values of the joint resistance lie in the range of 0.335–0.213 cm^2 °C/W which is an order of magnitude smaller than the joint resistances of a bare joint. If greases with thermally conductive ceramics are used, the joint resistance can be reduced to values below 0.065 cm^2 °C/W. The correlation equations are based on conforming rough surfaces with interstitial substances which perfectly wet all portions of the surfaces which form the gap. Any nonflatness will result in interfaces with larger gaps which will have larger joint resistances. If the interstitial substance does not perfectly *wet* the contacting surfaces, this will also produce a more thermally resistive interface. The correlation equations therefore correspond to the best thermal joints which have the smallest joint resistances. The use of other interstitial materials, such as thermal compounds, elastomers, or adhesive tapes has been shown to increase the complexity of the joint conductance problem significantly. In order to successfully solve this problem, simulation methods provided the way to model the complex interface phenomena. It is common practice for high-power applications to assemble power devices as bare dies in the chip on PCB or to use flip chip assemblies with a directly mounted copper or aluminum heat sink. The thermal resistance of the TIM is the bottleneck of the heat transfer from the active device junction to the cooler. Better TIMs are crucial to even out the localized hot spots (Yovanovich et al. 2004).

Criteria for Selection of Thermal Interface Materials

The TIM acts to connect the different thermal management components in electronic packaging. Formation of a small thermal barrier is an important property of a TIM. The thermal barrier can be described in terms of effective thermal resistance, or reverse effective thermal conductivity through the TIM which is preferably as high as possible. The effective thermal conductivity of the TIM is primarily due to the interfacial heat transfer coefficient as well as the intrinsic bulk thermal conductivity of the TIM. A variety of other properties are also important for a TIM depending on the particular application, for example, an ability to accommodate or avoid thermal expansion stresses when joining two materials, an ability to form a mechanically sound joint that is stable during thermal cycling, a lack of sensitivity to moisture and temperature changes, manufacturing feasibility, and low cost.

Figure 8.1 shows thermal barrier of thermal resistance across an interface with a TIM. After inserting a TIM between two contact solid surfaces, the effective thermal resistance, R_{TIM}, at the interface consists of the bulk resistance, R_{bulk}, of the TIM arising from its finite thermal conductivity, and the contact resistance, R_{c} between the TIM and the adjoining solids. Therefore, R_{TIM} can be expressed as (Prasher et al. 2003):

$$R_{\mathrm{TIM}} = \frac{BLT}{k_{\mathrm{TIM}}} + R_{\mathrm{c1}} + R_{\mathrm{c2}}, \tag{8.6}$$

where BLT is the bond-line thickness of the TIM, k_{TIM} is the thermal conductivity of the TIM, and R_{c1} and R_{c2} are the contact resistances of the TIM with the two adjoining surfaces. The sum of contact resistance of the TIM with the two adjoining substrates can be expressed as (Prasher et al. 2003):

$$R_{\mathrm{c}} = R_{\mathrm{c1}} + R_{\mathrm{c2}} = \left(\frac{\sigma_1 + \sigma_2}{2k_{\mathrm{TIM}}}\right)\left(\frac{A_{\mathrm{nominal}}}{A_{\mathrm{real}}}\right), \tag{8.7}$$

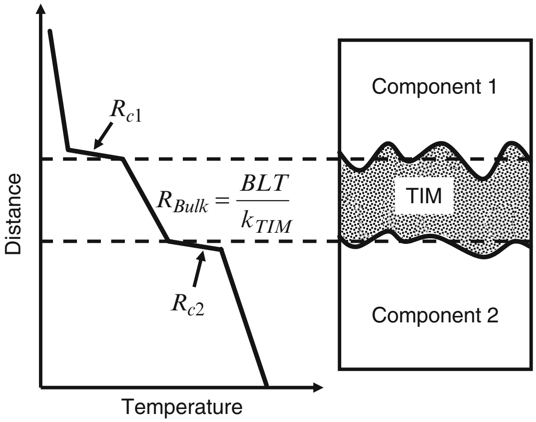


Fig. 8.1 Thermal resistance across an interface with a thermal interface material (TIM)

where σ_1 and σ_2 are the surface roughness of the substrates, A_{nominal} is the nominal area of heat transfer, and A_{real} is the real area of heat transfer. Therefore, minimization of contact resistance can be done through increasing pressure applied on the interface, decreasing surface roughness, increasing thermal conductivity of the TIM, and increasing capillary force by changing the surface chemistry.

One of the goals of thermal design is to reduce the thermal resistance R_{TIM}, which can be accomplished by reducing the BLT, increasing the thermal conductivity and reducing the contact resistances R_{c} (R_{c1} and R_{c2}). As the reduction of BLT may be limited in some cases, the two most desirable properties of a TIM are high thermal conductivity and high compliance in order to increase the thermal conductance and reduce the contact resistances. Only few homogeneous materials possess both these properties, such as indium and other solder alloys, therefore, TIMs are typically composite materials with metallic or ceramic fillers in a polymeric matrix. Typically used fillers such as alumina (Al_2O_3) or boron nitride (BN) are characterized by relatively high thermal conductivity and low compliance. Most matrix materials, e.g., silicone, have low thermal conductivity but high compliance. In view of practical applications, optimal volume fractions and geometric distributions of filler and matrix materials are sought at which the joint conductance assumes a maximum value. The optimal filler volume fraction is expected to depend on a series of factors, including the relative thermal and mechanical properties of the matrix and filler, the filler shape, its distribution, and orientation. Furthermore, the size of the filler particles relative to the thickness of the TIM layer will also affect the optimal filler volume fraction, as will the boundary resistance between filler and matrix (Singhal et al. 2004). As a result, the optimum property of the TIMs can be achieved through optimizing the volume fraction and the geometric distribution of filler particles for which the joint conductance of a rough surface-TIM-rough surface system takes the maximum value.

In practical applications, the criteria for selection of the TIMs can be summarized as shown below.

Thermal Conductivity of the Material

Thermal conductivity is the quantified ability of any material to transfer heat. The thermal conductivity of the interface material has a significant impact on its thermal performance. The higher the thermal conductivity, the more efficient the material is at transferring heat. Materials that have a lower thermal conductivity are less efficient at transferring heat, causing a higher temperature differential to exist across the interface. To overcome this less efficient heat transfer, a better cooling solution (typically, a more costly solution) must be used to achieve the desired heat dissipation.

Metallic TIMs usually have high thermal conductivity. For polymer based TIMs, the thermal conductivity of a TIM is typically enhanced by loading a soft, sometimes liquid-like polymeric material matrix with conducting solid particles, such as aluminum, alumina, and BN. If the design requirement is that the TIM should be thermally conducting but electrically insulating then the ceramic-based filler particles are more typically chosen. The bulk thermal conductivity of particle laden polymer-based TIMs can be functionally expressed as (Prasher et al. 2003):

$$k_{\mathrm{TIM}} = f(k_{\mathrm{f}}, k_{\mathrm{m}}, \varphi, R_{\mathrm{f}}), \tag{8.8}$$

where k_{f} is the filler thermal conductivity, φ, filler volume fraction, and R_{f} is the contact resistance between the fillers and the polymeric matrix. When $k_{\mathrm{f}}/k_{\mathrm{m}} \gg 1$, (8.8) can be expressed as (Prasher et al. 2003):

$$\frac{k_{\mathrm{TIM}}}{k_{\mathrm{m}}} = \frac{1}{(1-\varphi)^{3(1-\alpha)/(1+2\alpha)}}, \tag{8.9}$$

where α is the Biot number and is given as:

$$\alpha = \frac{R_{\mathrm{f}} k_{\mathrm{m}}}{d}, \tag{8.10}$$

where R_{f} is the interface resistance between the filler and the particle and d is the diameter of the particle. R_{f} could arise because of imperfect mixing of the particle with the polymer matrix, due to phonon acoustic mismatch, or due to a combination of the two phenomenon. The contribution due to phonon acoustic mismatch at room temperatures or higher is important only when the thermal conductivity of both the materials is very high. In the case of silicon oil-based TIMs, for instance, it is safe to assume the R_{f} is arising from imperfect wetting or mixing of the filler particles with the silicon oil, as the thermal conductivity of silicon oil is very low. Therefore, the phonon acoustic mismatch component is very low at room temperatures. The reason for higher R_{f} for 60% volume fraction could be due to difficulty in wetting the surface of the particle with the silicone oil as the volume fraction is so high.

Electrical Conductivity of the Material

Depending on the application requirement, the TIMs can be provided with electrically conductive or electrically insulated products. Some metallic TIMs such as solders, low melting alloys (LMAs), or metal-based compounds are electrically conductive, whereas ceramic-based compounds are typically not. Polymer-based composites can be both thermally and electrically conductive. Electrically conductive TIMs can be used for application that do not cause circuit shorting or intend to enhance electromagnetic interference (EMI) shielding performance. Electrically insulated TIMs are used to circuit short-sensitive cases. For example, metal-based thermal compounds are not hazardous to the processor die itself, but other elements on the processor or motherboard can be at risk if they become contaminated by the compound. For this reason, much of electronic packaging is not recommended in the use of electrically conductive TIM.

Spreading Characteristics of the Material

The spreading characteristics of the TIM determine its ability, under the pressure of the mounted heat sink, to spread and fill in or eliminate the air gaps between the processor and the heat sink. Because air is a very poor thermal conductor, the more completely the interface material fills the gaps, the greater the heat transference.

During spreading of the TIM, reaching a minimum BLT is often another parallel goal of thermal design. BLT is a function of various parameters such as application pressure (i.e., pressure applied in bringing the two contact surfaces together) and particle volume fraction. An empirical expression for the BLT of particle laden polymeric TIMs is (Prasher et al. 2003):

$$\mathrm{BLT} = 1.31 \times 10^{-4}\left(\frac{\tau_{\mathrm{y}}}{P}\right)^{0.166}, \tag{8.11}$$

where τ_{y} is the yield stress of the TIM and P is the applied pressure. This correlation was validated in the pressure range of 25–200 psi application pressures. Because the yield stress of the TIM increases with increasing filler loading, BLT is higher for higher volume fraction. Therefore, there are two competing effects with regard to filler loading for the thermal resistance of the TIM: k_{TIM} increases and BLT also increases with increasing filler volume fraction at the same pressure, which leads to an optimal filler loading for the minimization of R_{TIM} (Prasher et al. 2003).

Long-Term Stability and Reliability of the Material

The long-term stability and reliability of the TIM is its ability to provide a sufficient thermal conductance even after an extended time or extensive use of the electronic equipment (for example, servers or personal computers that work 24 h a day, 7 days a week). Low-quality compounds may harden or leak out over time (the pump-out effect), leading to overheating or premature failure of the processor. High-quality compounds provide a stable and reliable TIM throughout the lifetime of the processor. Thermal greases with higher viscosities are typically more resistant to pump-out effects on lidless processors. Another typical requirement of TIMs is that of reworkabilityBecause the heat sink is attached to the device by the OEM in a number of applications, reworkability is a requirement to avoid yield loss due to heat sink attach. Reworkability implies that the heat sink should be easily removed and that the TIM should be easily cleanable so that the heat sink may be reattached if needed. This requirement has led to certain classes of materials seeing continued popularity; e.g., filled greases, filled phase change materials (PCMs), and certain gels.

Ease of Application

A spreadable TIM-like grease requires the installer to carefully use the appropriate amount of material. Too much or too little material can cause problems. The PCM, for instance, has a fixed size and is therefore easier to apply in a consistent manner.

During materials design, apart from thermal requirements, the specific needs for the electrical insulation of electronic parts and other parameters, e.g., minimum distances and computer telephony integration have considerable impacts on the product design-in of TIMs. TIMs are therefore sometimes classified into electrically insulating or electrically noninsulating materials. Furthermore, parameters such as chemical consistence, proper surface properties for compensating surface deviations or mechanical tolerances, softness and flexibility, tensile strength, processability, easy handling and delivery shapes, and last but not least the economic efficiency among others must be considered when doing the product design-in. Environmental compatability, reworkability, suitability to adhesive coating, chemical, temperature and aging resistance, as well as life time and low outgasing of silicone are other important influences.

Table 8.1 shows some typical TIMs which have been developed and utilized in electronic packaging (Mahahan 2004). TIMs can basically be classified as metallic TIMs, conductive elastomer TIMs, thermal grease, phase-change materials, and emerging TIMs such as polymer solder hybrid (PSH), composite, or smart TIMs (Tong 2009).

TIMs are usually used on the following application areas of an electronic package: (1) to bring a bare die package into contact with heat sink hardware; (2) to bring the die into good thermal contact with an integrated heat spreader, and then to bring the integrated heat spreader into contact with system thermal solutions, such as chassis, heat sink, or OEM applied hardware. Conventionally, the TIM between the die or the die package and the heat spreader is called a TIM1, and the TIM between the heat spreader and the heat sink hardware is called a TIM2.

In addition, many applications call for TIM that can easily be placed on a chip, on a lid, or perhaps just against a heat source and a cooling solution contact plate. Metal foil with/without galvanic compatible surface plating, and compressible solder perform have been developed for such an application. The metal foil and compressible TIMs also fin the burn-in head to optimize their performance. The pressure range is around 35 to 100 psi. For instance, an indium foil preform offers uniform thermal resistance at lower applied stresses in compressed interfaces. The malleability of indium minimizes surface resistance and increases heat flow. This kind of TIMs delivers superior performance over time, they cannot experience

Table 8.1 Properties of typical thermal interface materials

Material type	Typical composition	Advantages	Drawbacks	Bond line thickness (mm)	Thermal conductivity (W/m K)
Grease	AlN, Ag, ZnO, Silicon oil	High bulk thermal conductivity, conforms to surface irregularities, no cure needed, reusable	Pump out and phase separation, migration	0.05	3–5
Gel	Al, Ag, Silicon oil, Olefin	Good bulk thermal conductivity, Conforms to surface irregularities before cure, no pump out or migration, reusable	Cure needed, lower thermal conductivity than grease	0.025–0.04	3–4
Phase Change Materials	Polyolefins, epoxies, polysters, acrylics, BN, Alumina, Al, Carbon nanotubes	Conforms to surface irregularities, no cure needed, no delamination, easy handling, reusable	Lower thermal conductivity than grease, no uniform bold line thickness	0.05–0.05	0.5–5
Phase change metallic alloy	Pure ln, ln/Ag Sn/Ag/Cu ln/Sn/Bi	High thermal conductivity, reusable	Complete melt possible, voiding	0.05–0.125	30–50
Solder	Pure ln, ln/Ag Sn/Ag/Cu ln/Sn/Bi	High thermal conductivity, easy handling, no pump out	Reflow needed, stress crack, delamination, Voiding possible Not reusable	0.05–0.125	30–86

pump out problems even under power cycling, and also resist bake out due to its solid state.

Metallic Thermal Interface Materials

The thermal conductivity of conventional polymeric TIMs generally does not exceed about 5 W/m K and is typically less than about 1 W/m K. However, metallic TIMs that form thermal interfaces with effective thermal conductivities of about 50 W/m K or greater will be the alternative to meet increasing thermal management requirement of high performance electronics. Most metallic TIMs may also exhibit a favorable solder or wetting behavior upon reflow which facilitates a low thermal interfacial resistance. During reflow, the solder and substrate are heated, the solder melts and wets by surface tension and/or local surface alloying. The interfaces consist of intermetallics or interdiffused metals with thermal properties that are frequently less desirable than those of the bulk TIM metal but much better than polymeric TIMs. In addition, the reflow or active bond process can also help to form reliable thermal interfaces. Metallic TIMs, however, can fail in certain applications as a result of the relatively large differences between the coefficients of thermal expansion (CTE) of the TIM and the semiconductor and/or heat sink components and the lack of compliance (Sreeram et al. 2003). To take advantages of the metallic TIMs and avoid their disadvantages, a large number of metallic TIMs have been developed and offered different characteristics for selection. Such metallic TIMs typically include reflow solders and active bond process, nonreflow solders and LMAs, composite solders, and hybrid metallic solder materials as well as gold–gold interconnection.

Reflow Solders and Active Bond Process

Reflow soldering is a process in which a solder TIM preform or TIM solder paste is used to attach one or several electrical components to each other, after which the assembly is subjected to controlled heat, which melts the solder, permanently connecting the interfacial joint. Heating may be accomplished by passing the assembly through a reflow oven or under an infrared lamp or by soldering individual joints with a hot air pencil. A thermal reflow process profile typically undergoes five transitions: (1) Preheat–brings the assembly from 25°C to preheat zone and evaporates solvents from solder perform or solder paste. A slow ramp-up rate will prevent any damage due to thermal shock. The time and temperature to evaporate the solvents will depend upon the solder perform or solder paste that is used. (2) Flux activation (preheat)–dried solder perform or solder paste is heated to a temperature in which the flux will react with the oxide and contaminants on the surfaces to be joined. The time and temperature should be long enough to allow the flux to fully clean these surfaces but not too long that the flux may be exhausted before soldering takes place. (3) Thermal equalization–achieves temperature equalization approximately 20–40°C below the peak reflow temperature. Time and temperature will depend on the mass and materials. (4) Reflow–in this stage, the assembly is briefly brought to the temperature sufficient to produce reflow of solder. (5) Cool down–this is the final stage in the solder process. Gradual cooling should be used. The end result should be as fast as possible without causing thermal shock to the components. Cool down in this manner will produce a finer grain structure in the solder joint, which will yield a more fatigue-resistant solder joint.

Although each offers different thermal and mechanical properties, reflow solders are very attractive for use as a TIM because they have high thermal conductivities ranging from 30 to 86 W/m K. The key to using solder TIMs is to reduce voiding during reflow when assembling or mounting the components together. Unlike polymer- or grease-based materials used for thermal interfacing, solder voids will not propagate later during use due to pump out or migration, which assures a higher end of life performance. Thermal solders provide the best physical connection of all TIMs. Using solder eliminates the issue of bleed-out from the thermal greases while providing very good adhesion. This mechanical attachment is a particular advantage when external clamping is not feasible. To take advantage of these properties, interfaces and assembly are designed to ensure proper wetting of the contact surfaces, which minimizes voiding. Furthermore, thermal expansion of components in a thermal assembly may stress solder TIMs. For this reason, brittle alloys should not be used as TIMs. Bismuth-containing alloys are especially poor choices because of their low thermal conductivity and brittle nature. Au–Sn alloys handle stress well, although they may not be soft enough for some applications where the heated materials expand at markedly different rates. It is important to choose a solder that will be able to compensate for CTE mismatch. Design of the solder thermal interface requires understanding the interconnect materials to minimize the effects of intermetallic formation and performance degradation. Additionally, the solder must provide for the compliance of the thermal expansion mismatch between the semiconductor and the heat sink. Regarding interface compliance, indium may be the best solder to use as a thermal interface. Pure indium metal provides a unique combination of high conductivity (86 W/m °C) and compliance (60 psi shear flow stress and no work hardening). Indium is applied in the mechanical sealing of metallic and nonmetallic surfaces with excellent integrity. Because indium will wet to nonmetallic substrates, it is especially well suited for use against many materials that are commonly used in semiconductor packages. This mixture of properties makes indium uniquely suited to thermal interface solutions with or without reflowing. Indium can also be cold welded in applications where normal soldering temperatures are detrimental to the electronic packaging.

In fact, as a Pb-free solder-based TIM, indium has been successfully and commercially used to meet the increasing demand for thermal cooling capability of electronic packaging. Figure 8.2 gives an example of indium as a TIM1 to connect the silicon die and the heat spreader together (Renavikar et al. 2008). To assemble the indium TIM1 appropriately, the following issues need to be paid attention: (1) effectively reduce the thermodynamically stable native indium oxide on the indium TIM1 perform; (2) to control solder joint voiding post joint formation; (3) to control interfacial reactions with surface finishes on the heat spreader lid and the back side metallization on the silicon die; and (4) to deal with reliability issues faced in small and large die products, such as thermal fatigue cracking of the indium during thermal cycling. The assembly process, including the reflow of the indium TIM1 to form uniform intermetallic compounds post assembly, is a key challenge. The indium oxide on the surface of the indium needs to be effectively reduced in order to form uniform and defect-free intermetallic layers at both the die/indium and the heat spreader lid plating (Ni/Au) and the indium (In). Indium oxide is an extremely tenacious and thermodynamically stable oxide. The presence of voiding in the joint can potentially lead to an increase in local thermal resistance and consequently lead to the degradation of the thermal performance of the joint. Additionally, excessive spallation of the

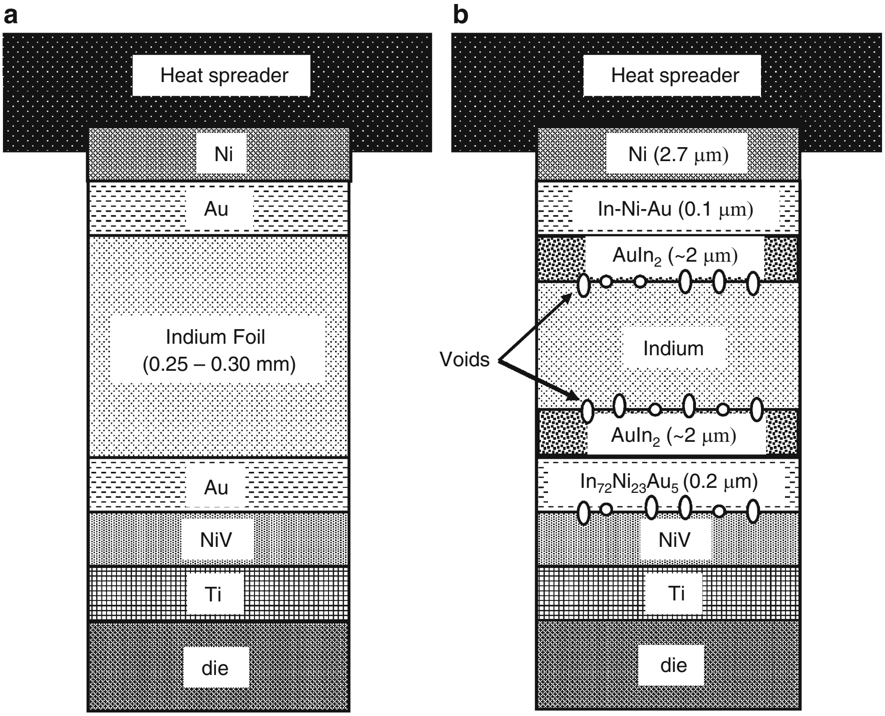


Fig. 8.2 Use of indium as TIM1 and interactions with surface finish on heat spreader and back side metallization on the die (**a**) pre- and (**b**) post-reflow assembly

binary Au–In intermetallic compound as well as the formation of excessive Kirkendall voiding due to relatively different diffusion coefficients of In–Au and Ni can result in an increase in the thermal resistance of the joint. The reliability performance of the joint can be modulated by the relative thickness and morphology of the binary and ternary intermetallic compounds as influenced by the fluxing ability of the flux used and the reflow profile used, as well as mechanical design attributes of the heat spreader dimensions/die size, package stiffness, and preform dimensions (Renavikar et al. 2008).

Other reflow solders that might be used for TIMs are shown in Table 8.2. Generally, next-generation solder TIMs should meet the following requirements: High reliability over a wide application and product design range; high process yields with existing processing equipment; compatibility with the fabrication needs for various solder forms; low toxicity; and low cost. One thing which will probably never change is the need for good solder wetting and spreading. This requires that the solder exhibit a low viscosity and low surface tension, and a sufficiently high dissolution rate of base metal or metallized surface finishes into the molten solder. Rapid formation of intermetallic compounds is also desirable, at least in the initial stage because it tends to lower the free energy of the system,

Table 8.2 Reflow solders that might be used for thermal interface materials

Type of solder alloys	Composition (brand name)	Melting point (°C)	Thermal conductivity (W/m K)	CTE (ppm/°C)	TIM format
In and its alloy	Indalloy 4	157	86	29	Paste/preform
	100ln	157	84	32.1	Paste/preform
	21.5ln16Sn62.5Ga	10.7	35.0	–	Paste/preform
	51ln16.5Sn32.5Bi	60	–	–	Paste/preform
	66ln34Bi	72	40.0	–	Paste/preform
	52ln48Sn	118	34.0	–	Paste/preform
	97ln3Ag	143	73.0	–	Paste/preform
Sn and its alloy	42Sn58Bi	138	18.5	14	Paste
	63Sn37Pb	183	50.0	–	Paste/preform
	96.5Sn3.5Ag	221	33.0	–	Paste/preform
	100Sn	223	73.0	22	Paste/preform
	80Au20Sn	280	57.0	–	Paste/preform
Active bond solders	SB115 (ln/Sn+Ti)	115–120	–	–	Preform
	SB140 (Bi/Sn+Ti)	135–150	–	–	Preform
	SB220 (Sn/Ag+Ti)	190–232	48.0	19	Preform
	SB400 (Zn/Al+Ti)	390–415	80.0	32	Preform

and thereby promotes the further spread of solder. High-tin alloys, for instance, are adequate for viscosity, dissolution rate, and intermetallic formation rate requirements, but unfavorable due to the relatively high surface tension of tin. The latter may be improved with doping of some surface-active, low-surface energy elements. Good oxidation resistance of the solder will also be needed because formation of the oxide during soldering immediately impedes the spreading process. The oxidation resistance can often be enhanced by doping with an element such as P, Ge, or Ga.

As shown in Table 8.2, a group of novel active bond solders have been developed and enable wetting directly to metal and ceramic surfaces without the need for flux. This is achieved through the modification of conventional solders by the addition of titanium (0–5%) and/or rare earth elements. These active elements migrate to the interface and react with the opposing material surface to remove oxides and nitrides and transport them into the bulk of the solder as an inert material. This process can be conducted in an air environment but requires the application of a low-level mechanical shearing action to break a thin oxide (Sn–Ti) layer on the molten solder and initiate the reaction with the component interfaces. The level of shear is claimed to be small and can be delivered by brushing or scraping the surface, sliding the joining surfaces relative to one another, or by the application of high frequency vibration to the parts to be joined. Once the oxide layer has been disrupted, the bulk solder reacts very rapidly with the substrate surfaces to form either a metallurgical (metals) or atomic attraction/van der Waals bond. The bonding procedure is typically as follows (Young et al. 2006):

(1) Heat substrate surface to 250°C (solder material dependent), typically the process is conducted at 10–20°C above the melting point of the solder. The molten active solder would retain the ability to self align components
(2) Attach the solder preform and establish layer of material on the surface
(3) Use ultrasonic tool or mechanical action to apply enough solder on one surface to fill gap between the die and the heat spreader lid
(4) Bring lid and die together to minimize trapped air and load with ~2 lb/in^2
(5) Cool to below 190°C. The optimum bond line thickness for these active solders is 50–100 μm compared with 200–250 μm for conventional die attach solders

Thicker layers result in degraded performance. The mechanical performance of active solder material is similar to comparable conventional solders, although the addition of titanium is to improve the high temperature creep performance of Sn–Ag–Cu alloys. Mechanical strength will be dependent on the substrate materials and the joint design. In general, metallurgical bonds achieve 20–55 MPa (3,000–8,000 psi), and those employing van der Waals forces 6–12 MPa (1,000–2,000 psi). Silicon bonded to substrates has been shown to survive thermal cycling tests (1,000 cycles for -55°C to +125°C) and multiple solder reflow cycles (~260°C). The ability to join graphite and aluminum foams to metal-based plates opens up the potential of replacing some fin-plate heat exchangers. Thermal property (heat transfer coefficient in closed loop water) measurements showed graphite-foam samples to possess superior heat transfer coefficients compared with commercial aluminum fin-plate heat exchangers, having heat transfer coefficients between 10,000 and 20,000 W/m^2 K compared with 500–1,200 W/m^2 K for commercial aluminum fin-plate designs, thus demonstrating active solder joined graphite-foam cores to be a factor of over 15 times better. Comparative investigations on active-solder joined aluminum-foam cores resulted in coefficient values of 1,500–2,000 W/m^2 K. The potential benefits of active soldering are no flux, eliminates cleaning and residual corrosive material, no preplating, reduction in thermal impedance layers, reduction in process steps/cost, ability to solder a wide range of materials, good thermal/electrical joint conductivity, reworkable joint, high surface tension (low flow), and low penetration into foam materials and pipes/channels (Young et al. 2006).

Active soldering is a relatively new process and consequently is still developing a market presence. The active bond solder is potentially an attractive product for electronic thermal management systems. Two key features are: (1) ability to directly join combinations of high thermal conductivity materials with a reduced number of interface (thermal impedance) layers; and (2) clean (no-flux) processing. The latter is becoming increasingly important as package density increases, systems become more complex, and environments more severe. The process is relatively immature and consequently new applications will need to be fully tested to establish the performance of the joint and its impact on the application and product reliability. The need to precoat materials prior to soldering may limit some high-volume applications unless alternative metallization techniques, such as sputtering can be developed.

Nonreflow Solders and LMAs

Nonreflow solders indicate phase change metallic alloys, also called LMAs, typically including alloys of indium, bismuth, gallium, tin, or silver. They are in liquid phase at operating temperatures; typical-phase change occurs between 60 and 80°C. Because LMAs are all-metal they contain no organic materials and hence require no curing during application. The superior performance of LMAs as TIMs is a result of the thermally conductive nature of metals and the high degree of wetting they enjoy. Good wetting means low contact resistance and allows relatively thin bond lines. These alloys are well suited as a thermal interface between materials of dissimilar CTEs, however, reliability problems in production implementations and resulting catastrophic failure have retarded their adoption. Mechanical problems include shake-out due to mechanical shock and drip-out due to low viscosity, especially with vertically oriented interfaces. Thermal problems include dry-out caused by thermal cycling leading to the creation of voids in the interface and catastrophic failure; the growth of thermally resistive intermetallic compounds through interfacial contact, and oxidation/corrosion in nonhermetically sealed applications, both leading to a steady decrease in performance and eventual thermal failure (Macris et al. 2004).

Many alloy combinations can be classified as LMAs for TIM applications. Alloys which possess a liquidus point below the operating temperature of the electronic component are needed to allow the LMA to adequately flow into all surface asperities of the interface. In general, alloys comprised of the fewest number of constituents possess the highest thermal conductivities. Common LMA candidates include bismuth-based or gallium-based alloys as depicted in Table 8.3. Liquid metals, such as alloys of bismuth, gallium, and indium potentially offer both low interfacial resistance and high conductivity. Several alloys of gallium with very low melting points have also been identified as potential liquid metal interface materials. Thermal performance of such an interface would be more than one order of magnitude greater than many adhesives typically in use. Several very low melting point gallium-based alloys are liquid at room temperature. These gallium-based alloys are finding increased use in various applications as a replacement for toxic mercury, which has a high vapor pressure at room temperature. These alloys have reduced toxicity and lower vapor pressure than mercury.

Alloy systems that are liquid at room temperature have a high degree of thermal conductivity far superior to ordinary nonmetallic liquids. This results in the use of these materials for specific heat conducting and/or dissipation applications. Other advantages of these liquid alloy systems are their inherent high densities and electrical conductivities. These alloys will wet most metallic surfaces once oxides have been sufficiently removed from the substrate surface. However, gallium is very reactive with some metals, even at room temperature. At high temperatures, gallium dissolves most metals, although a number of them, including Na, K, Au, Mg, Pb, Ni, and interestingly Hg are only slightly soluble at moderate temperatures. Gallium and the gallium alloys, like gallium–indium, have the ability to wet too

Table 8.3 Typical low melting alloys

Low melting alloys	Liquidus (°C)	Solidus (°C)
61Ga/25ln/13Sn/1Zn	7.6	6.5
62.5Ga/21.5ln/16.0Sn	10.7	10.7
75.5ga/24.5ln	15.7	15.7
95Ga/5ln	25.0	15.7
100Ga	29.78	29.8
44.7Bi/19.1ln/6.3Sn/22.6Pb/5.3Cd	47.2	47.2
49Bi\21ln\12Sn\18Pb	58	58
32.5Bi\51ln\16.5Sn	60	60
49Bi\18ln\5Sn\18Pb	69	58
33.7Bi/66.3ln	72	72
57Bi/26ln\17Sn	79	79
54.02Bi\29.68ln\16.3Sn	81	81

many nonmetallic surfaces such as glass and quartz. Gently rubbing the gallium alloy into the surface may help induce wetting.

Typical applications for these materials include thermostats, switches, barometers, heat transfer systems, and thermal cooling and heating designs. Uniquely, they can be used to conduct heat and/or electricity between nonmetallic and metallic surfaces. Alloys are packaged in polyethylene bottles and shipped in accordance with applicable US federal regulations. Unopened bottles have a guaranteed 1-year shelf life. As the alloy is removed from the bottle, the volume can be replaced with dry aragon, which will minimize the possibility of oxidation at the surface of the alloy. If the alloy has been stored below its melting point and has solidified, it should be remelted and thoroughly shaken or mixed before use. Care should be taken in reheating the alloy in the original packaging provided. Temperatures should not exceed 65.6°C.

Although LMAs offer both low interfacial resistance and high conductivity, they have historically suffered from various reliability issues including: corrosion/oxidation, intermetallic formation, drip-out, dewetting, and migration. Unless mitigated, these mechanisms will continue to degrade the interface, resulting in a thermally related catastrophic failure of the actual electronic component.

Corrosion, considered to be the main failure mechanism in LMA materials, is driven primarily by moisture, oxygen, and heat. The liquid phase of these alloys at operating temperatures facilitates rapid diffusion, accelerating the corrosion process. Corrosion of an LMA is primarily an electrochemical process in which surface atoms of the alloy react with a substance in contact with the exposed surface. Electricity passes from a negative region to a positive region (both on the LMA) through an electrolyte or corroding medium. In the typical electronics environment, the corroding medium is liquid or vapor phase moisture. Moisture films on an LMA may contain dissolved substances which affect corrosion such as oxygen, various oxides/dioxides, sulfates, chlorides, and metal ions. Corrosion may also be accelerated by galvanic effects which operate by a difference in potential between dissimilar metals. As most LMA combinations lie near the anodic end of the galvanic series, the LMA will preferentially corrode when in contact electrically with a metal of higher cathodic potential and an electrolyte. Many current flip chip packages do not contain a lid seal, but instead use a partial bead of adhesive to allow venting of the package cavity. The die underfill provides all the moisture protection needed. To provide adequate LMA moisture protection, the package cavity must be of a closed configuration. The longest package lifetimes will be obtained with epoxies, or alternatively sealants being developed for near hermetic microelectromechanical system packaging. By providing a near hermetic seal between the package lid and package laminate, corrosion due to moisture films can be significantly reduced (Macris et al. 2004).

Mechanical stability should be considered due to the fact that liquid metals flow quite well. This characteristic alone poses some special challenges to overcome if they are to be used successfully as a TIM. A wire mesh has been incorporated in the thermal interface to control excess LMA, and making a paste of the LMA by incorporating various materials in particulate form to increase viscosity and reduce migration. The solid structures or phases proposed for incorporation within the thermal interface address the basic problem of getting an LMA to stay put when in service. These structures increase the surface contact area with the LMA in the thermal interface. As long as the total solid–liquid interface energy is less than the interface energy of the liquid–gas and solid–gas interfaces it replaces, the LMA will minimize its surface energy by wetting the surfaces within the interface. The LMA may still wet the surface adjacent to the thermal interface if it is the same wettable surface used under the die, particularly when acted upon by an additional force. Additional forces will arise from shock, vibration, and CTE mismatches between the LMA and other components. Once the LMA has wet the surface adjacent to, but outside the thermal interface, it is doubtful surface tension alone will retain it within the interface when acted upon by external forces. Others have proposed addressing this difficulty with gaskets to contain the LMA and fillers or noneutectic (slushy) compositions to increase its viscosity. Another simple way is to deploy the liquid metal in closed cavities where no opportunities for shorts or adverse reactions with other metals exist (Macris et al. 2004).

Designing an LMA thermal interface system has similarities to designing a solder joint system. As with a solder joint system, no deleterious intermetallics must form at the liquid solid interfaces of the LMA system. For the LMA system, deleterious intermetallics will be any having poor thermal conductivity that grow thick enough to decrease performance during the life of the component. The possibility of intermetallic formation for a given metals system can be determined from the binary equilibrium phase diagrams for the various metals present, but finding thermal conductivities for most intermetallics in the literature will be unlikely, and finding parameters necessary to calculate growth rates for them is even less likely. Consequently, for a system where intermetallics are likely to form as indicated by the phase diagram, systems will need to be aged at elevated temperature, thermal performance will need to be tested periodically, and if a decrease in thermal performance is observed, cross sections will need to be prepared to identify the offending intermetallic so it may be eliminated. Systems containing gallium pose additional challenges. Gallium metal is quite corrosive to other metals (including aluminum and copper) because of the rapidity with which it diffuses into the crystal lattices of metals. The few metals that tend to resist attack are molybdenum, niobium, tantalum, and tungsten. To prevent amalgamation with another metal, a nonreactive coating such as Teflon, siloxane, hydrogenated carbon, or thin ceramic layers may be applied to the interfaces. Additionally, refractory metals possessing good thermal performance and chemical inertness may be deposited. Anodized/oxide or conversion coatings can also provide the necessary chemical stability for various LMA compositions (Macris et al. 2004).

These challenges should be mitigated by applying a multidisciplinary approach. Therefore, LMA alloys can be applied as a TIM offering superior thermal performance due to their high thermal conductivities and low contact resistance, resulting from excellent surface wetting. Reworkability, ease of handling, and a lack of cure make this attractive in a high-volume setting.

Composite Solders and Hybrid Metallic Thermal Interface Materials

Next-generation electronic packages need highly conductive TIMs dominated by solder or metallic TIM1. Some solder TIMs, such as AuSn and indium, have been developed and commercialized successfully. The eutectic gold–tin alloy is 80Au/20Sn with eutectic of 280°C (556°F) and is reflowed in a pure nitrogen or forming gas atmosphere with fluxless soldering, normally onto gold-based metallizations. The peak reflow temperature is usually 320–340°C in a bell-shaped profile, with a dwell time at peak temperature of 2–3 min, and a total cycle time of 20–30 min, depending on the thermal load in the furnace/chamber. The solder provides excellent wetting characteristics (zero wetting angle with Au metallization), great joint strength ($\sim$275 MPa), superior resistance to corrosion, and high thermal conductivity (57 W/m K), making it the material of choice in many high-reliability applications, such as microwave, medical, and aerospace systems. However, the high cost and high reflow temperature have limited its commercial applications as a TIM.

As one of most promising TIMs, indium has been successfully commercialized. However, its limitation is also apparent: high cost; limited supply (80–100 tons/year); poor corrosion resistance; best used to temperature sensitive components that do not require high joint strength; and will not be exposed to harsh or high-stress environments.

With enhanced thermal performance, hybrid or composite metallic TIM1 is promising to replace indium or other TIMs for high-power microprocessors. The design concept of advanced hybrid metallic TIM1 materials would focus on: (1) low cost and ease of use; (2) compatible with current and future heat spreading systems; (3) improved thermal performance and reliability superior to current TIM1 materials, such as thermal grease, PSH, phase change metal alloy, and indium solder. Advanced metallic TIM1 can be formed via combination of solder pastes with thermal and hybrid reinforcements (such as powder, fiber, cloth, and screen or foam of metals, shape memory alloys, ceramics, and carbon materials, etc.). It will be suitable for high volume production, the metal or other highly conductive reinforcement will provide high thermal conductivity, and the reliable metallurgical bonding interface will result in low-contact resistance.

Materials selection of hybrid TIM1 depends on application requirements: performance, reliability, manufacturing process, cost, and flexibility. Major factors include:

(1) Melting point–satisfy assembly constraints.
(2) Thermal conductivity–the higher the better.
(3) Corrosion resistance–critical for nonhermetic packages.
(4) Strain-hardening exponent–influence thermal fatigue life due to CTE difference.
(5) Solubility of surface finish elements–relative high solubility benefits good bonding and controllable formation of intermetallics.
(6) Oxidation effect–oxidation both to solder and surface finish is negative for bonding and thermal fatigue life.
(7) Selection of surface finishes including barrier and bonding layers: the selection of barrier layer needs to consider dissolution time, wetting time, durability against corrosion, selective etchability, and the bonding layer is ensuring good adhesion, oxidation resistance, and high solubility in solder.
(8) TIM1 thickness (BLT) determination: (a) based on thermal and mechanical requirements; (b) thin BLT is good for heat transfer, while the thick BLT reduces stresses and increases compliance; (c) optimum BLT based on the balance of the thermal and mechanical requirements.
(9) Fatigue resistance can be enhanced by (a) reduce TIM1 area; (b) increase TIM1 thickness; (c) match Si die CTE with that of heat spreader.

The possible fabrication and attachment assembly processes of hybrid TIMs are shown in Figure 8.3. Figures 8.4 and 8.5 give examples of Option 1. The TIM format can be paste fabricated with a mixture of solder, flux, and filler. The solder powder is chosen with a melting point of 70–200°C. The flux can be (1) no-clean (NC) flux, which consists of rosin, solvent, and a small amount of activator; (2) water soluble (WS) flux that consists of organic acids, thixotrope, and solvent. The fillers include highly conductive metals, ceramics, or graphite and other materials; low CTE materials or shape memory alloys; and active interface bonding materials.

Figures 8.6 and 8.7 provide the constitutional sketch and the example of option 2 hybrid materials. The TIM format can be paste; paste plus screen/cloth preform; pad or tape; or combospreader (spreader attached with TIM1). The constitution includes (1) solder powder with melting point of 70–200°C; (2) flux can be (a) NC flux consists of rosin, solvent, and a small amount of activator, (b) WS flux consists of organic acids, thixotrope, and solvent; (3) selectable fillers: highly conductive metal, ceramics or other materials; low CTE

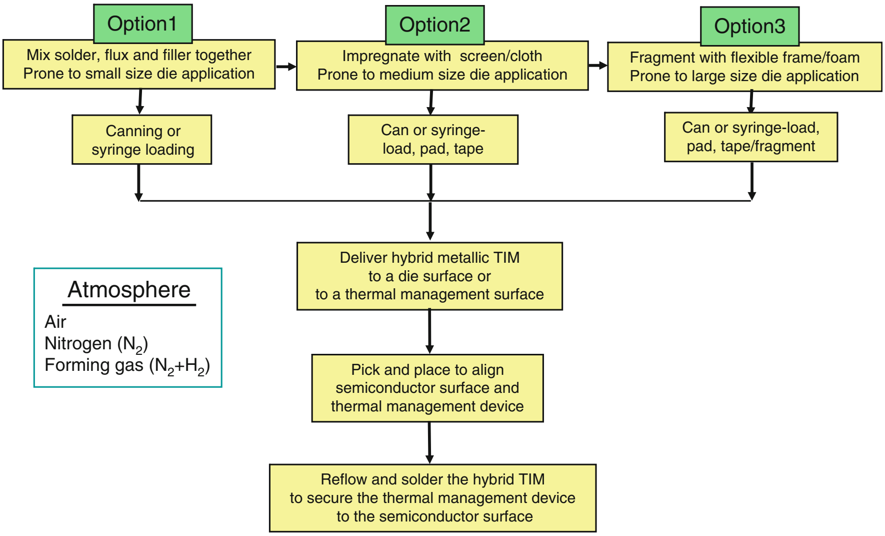
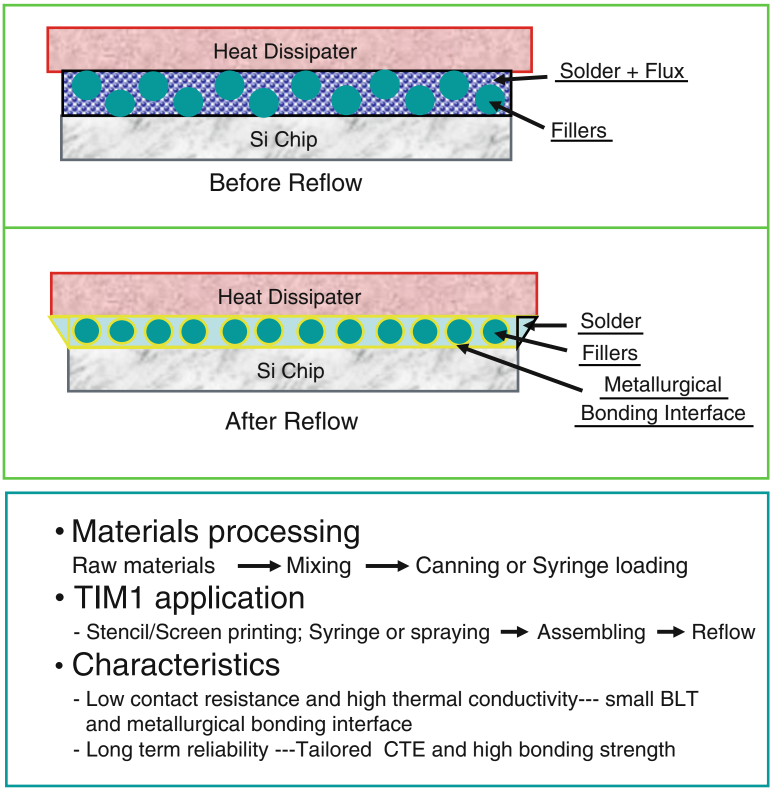


Fig. 8.3 Sketch of possible fabrication and attachment assembly processes for hybrid thermal interface materials



- Materials processing
  Raw materials → Mixing → Canning or Syringe loading
- TIM1 application
  - Stencil/Screen printing; Syringe or spraying → Assembling → Reflow
- Characteristics
  - Low contact resistance and high thermal conductivity--- small BLT and metallurgical bonding interface
  - Long term reliability ---Tailored CTE and high bonding strength

Fig. 8.4 Option 1–Hybrid metallic TIM1 paste for small die (<100 mm^2) application

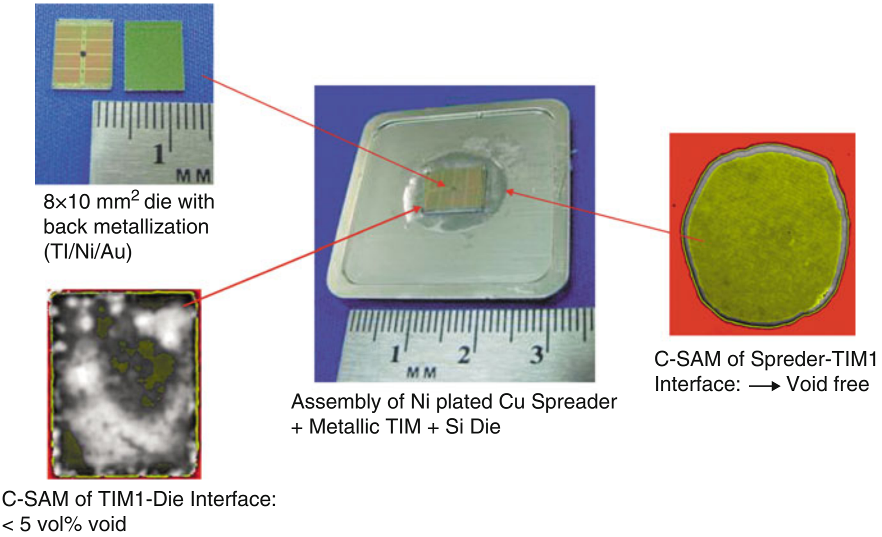


Fig. 8.5 Option 1–Example of metallic TIM1 for small die (<100 mm^2) application

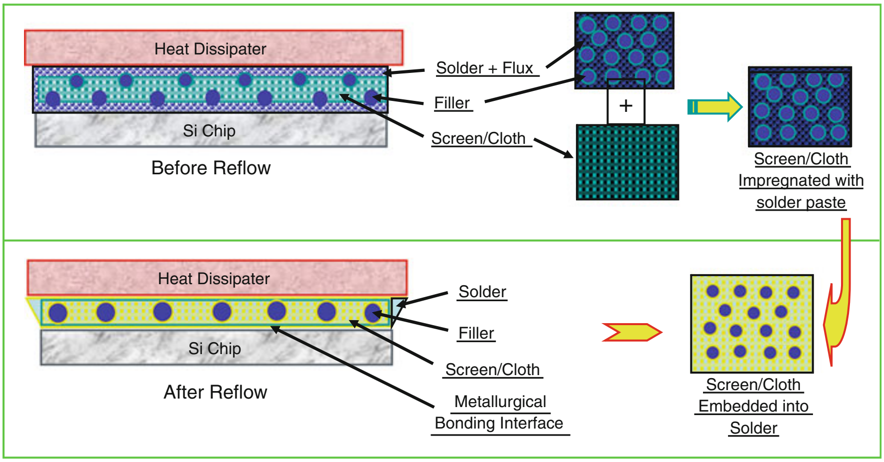


Fig. 8.6 Option 2–Hybrid metallic TIM1 for medium-sized die (100–200 mm^2) application–schematic of hybrid metallic TIM1(metal screen + solder with or without filler)

materials or shape memory alloys; active interface bonding materials; and (4) screen/cloth–metal or other highly conductive materials. TIM1 processing can be impregnating screen/cloth with solder paste by brushing, dipping, printing, and spraying, etc. TIM1 application is through selecting appropriate process depended on the TIM1 format. The major characteristics of the TIM include

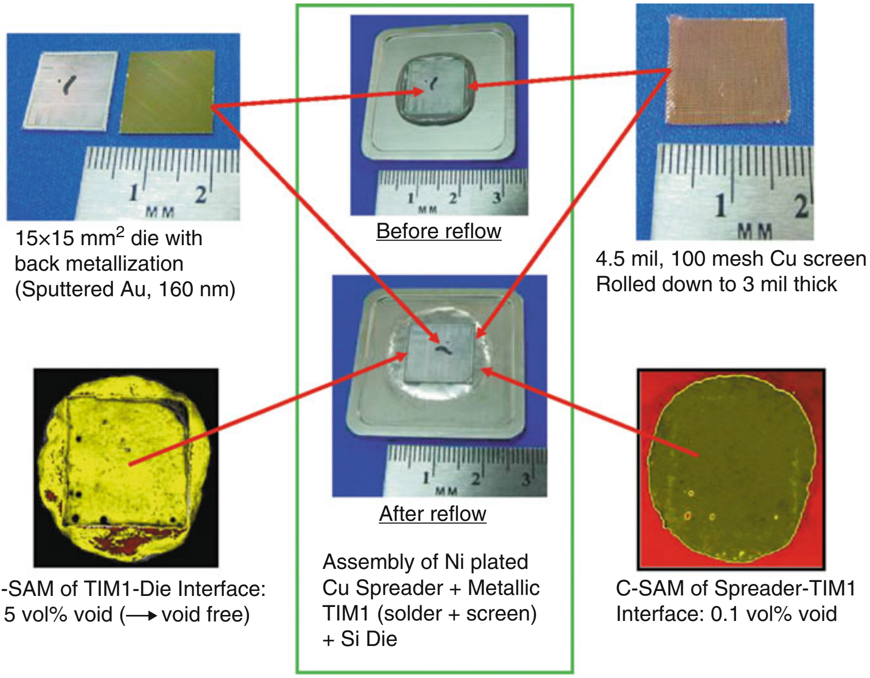


Fig. 8.7 Option 2–Example of hybrid metallic TIM1 for medium-sized die (100–200 mm^2) application–schematic of hybrid metallic TIM1 (metal screen + solder with or without filler)

(1) low contact resistance and high thermal conductivity with highly conductive screen/cloth and metallurgical bonding interface; (2) long-term reliability with tailored CTE, medium BLT, and high interface bonding strength.

The illustration of Option 3 hybrid thermal materials is shown in Figures 8.8 and 8.9. The TIM format can be paste plus the conductive frame; paste plus conductive screen/cloth preform and plus frame; pad or tape; combospreader (spreader attached with TIM1). Materials can be chosen from solder powders with melting point of 70–200°C. Flux can be chosen from NC flux consists of rosin, solvent, and a small amount of activator; or WS flux consists of organic acids, thixotrope, and solvent. Selectable fillers can be highly conductive metal, ceramics, or other materials such as low CTE materials, shape memory alloys, and active interface bonding materials. Selectable screen/cloth can be metal or other highly conductive materials. Selectable flexible frame/foam can made of polymer, carbon, ceramic, metal, composite, or other flexible frame/foam. TIM1 processing includes framing and impregnate screen/cloth with solder paste by brushing, dipping, printing, and spraying, etc. TIM1 can be applied through selected appropriate process depended on the TIM1 format. Major characteristics of the TIM include low contact resistance and high thermal conductivity; adjustable BLT, highly conductive filler,

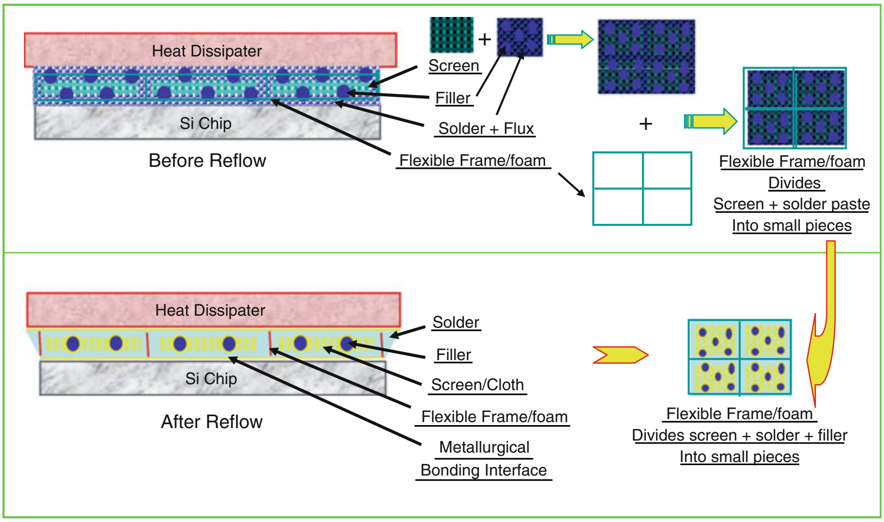


Fig. 8.8 Option 3–Hybrid metallic TIM1 for large-sized die (>200 mm^2) application–schematic of hybrid metallic TIM1 (frame + solder + filler + screen)

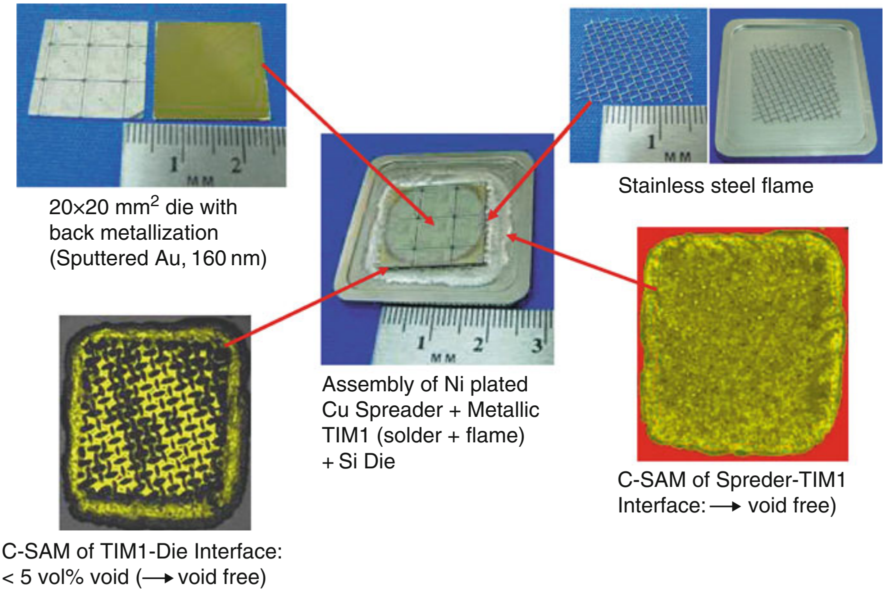


Fig. 8.9 Option 3–Example of hybrid metallic TIM1 for large-sized die (>200 mm^2) application–schematic of hybrid metallic TIM1 (frame + solder + filler + screen)

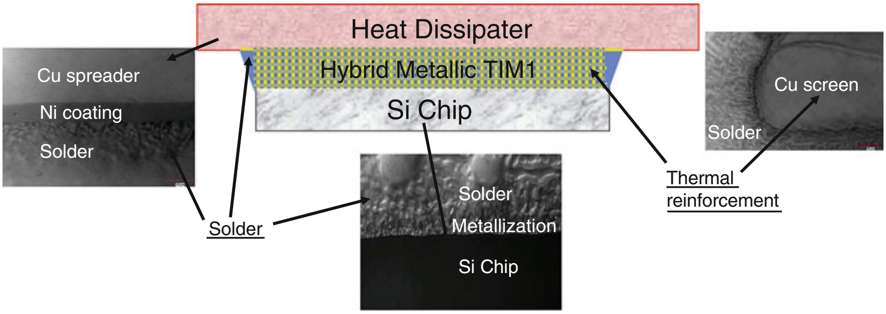


Fig. 8.10 Structure of hybrid thermal interface material and attachment assembly

screen/cloth, as well as metallurgical bonding interface; long-term reliability; framing TIM1 into smaller pieces to reduce interface shear strength, tailored CTE, adjustable BLT, and high interface bonding strength.

Figure 8.10 shows another option using rolling-cladding of solder and metal wire screen to form the hybrid metallic TIM and its constitutional structure attachment to the components of electronic packaging. The goal is to enhance bulk thermal conductivity and thermal fatigue life through construction of a solder system reinforced with highly conductive and high-reliability network. Flexible solder formulation provides low cost and good manufacturability. Near void-free metallurgical bonding interface maintains low contact resistance and strong adhesion. The basic design criteria include (1) thermal resistance competes with indium: TI < 0.025 °C cm^2/W at 4–5 mil; (2) capability to fabricate into multiple formats, such as dispensable paste, preform or tape and combo heat spreader attached with metallic TIM1; (3) reliability to meet or exceed industry standards: thermal cycling, highly accelerated stress test (HAST), high-temperature aging; and (4) Flexibility to optimize formulations for different package applications with the conformability to different die sizes and board materials or components.

The candidate solders used for the hybrid TIMs are shown in the Table 8.4. The Sn–Bi system is most competitive in cost and cost volatility, and particularly interesting with doping of Zn, Cu, and Sb elements. The Sn–Bi phase diagram is shown in Figure 8.11; the Sn–Bi system has the good melting point match for TIM1 application. Sn–Bi doped with Zn, Cu, Sb, etc. would refine grain size, induce uniform dispersion of fine precipitates, and slow coarsening of eutectic Sn–Bi. A combination of high mechanical strength and good ductility is likely to yield improved fatigue resistance properties; also a benefit to manufacturability when utilizing thermomechanical processes, such as rolling, pressing, etc. Figure 8.12 shows microstructure of casting and rolled Sn–Bi solders. The solders showed ductility that was quite good. One Cu wire screen was placed between two rolled solder sheets, and then rolled or pressed together to bond and form into a kind of hybrid metalic TIM, as shown in Figure 8.13. The C-mode scanning acoustic microscope showed that no apparent porosity presented in the laminate before and after reflow, which exhibited a good bonding between the solder and the copper wire

Table 8.4 Candidate solders used for the hybrid thermal interface materials

Type of solder alloys	Melting point (°C)	Remark
Indium	156.6	Baseline and current commercial TIM1
Sn30In5Zn0.5Cu	114–156	Indium reduces melting point and provides conductivity. Zn, Cu refine microstructure.
Sn3.5Ag8In3.5Bi1Zn	203	Eutectic Sn–Ag doped with Zn would exhibit good mechanical strength and creep resistance, due to refined microstructure. In reduces melting point. Bi further lowers the melting point and improves wettability
Sn58Bi	139	Low cost, simple eutectic
Sn45Bi1Zn0.5Cu	142–158	Sn–Bi doped with Zn, Cu has refined equiaxed grain structure. It can be quite ductile and may exhibit superplastic behavior.
Sn50Bi1Zn0.5Cu	138	Sn–Bi doped with Zn, Cu has refined equiaxed grain structure. It can be quite ductile and may exhibit superplastic behavior.
Sn35Bi1Zn0.5Cu	139–178	Sn–Bi doped with Zn, Cu has refined equiaxed grain structure. It can be quite ductile and may exhibit superplastic behavior.
Sn56Bi2Al	144	Al may provide strength and conductivity.
Sn45Bi1Zn1Mg	142–173	Mg may improve wettability, for flux-free application.
Sn45Bi1Zn1Sb	142–170	Zn, Sb effectively refine microstructure.

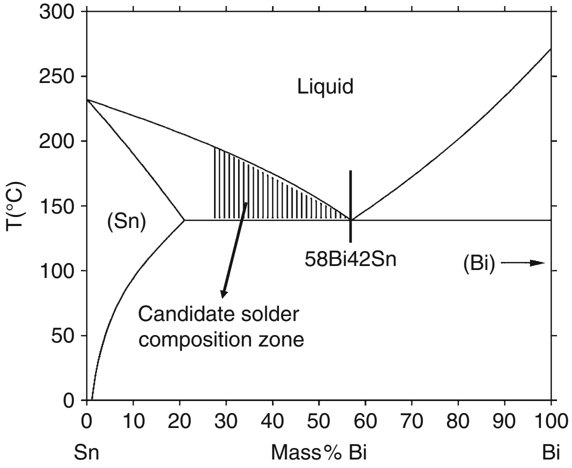


Fig. 8.11 Phase diagram of Sn–Bi

screen, and the forming process is feasible. The thermal resistance of the hybrid metallic TIM was tested using method as shown in Figure 8.14. The joint resistance is defined by

$$R_j = R_{c,1} + R_{bulk} + R_{c,2}. \tag{8.12}$$

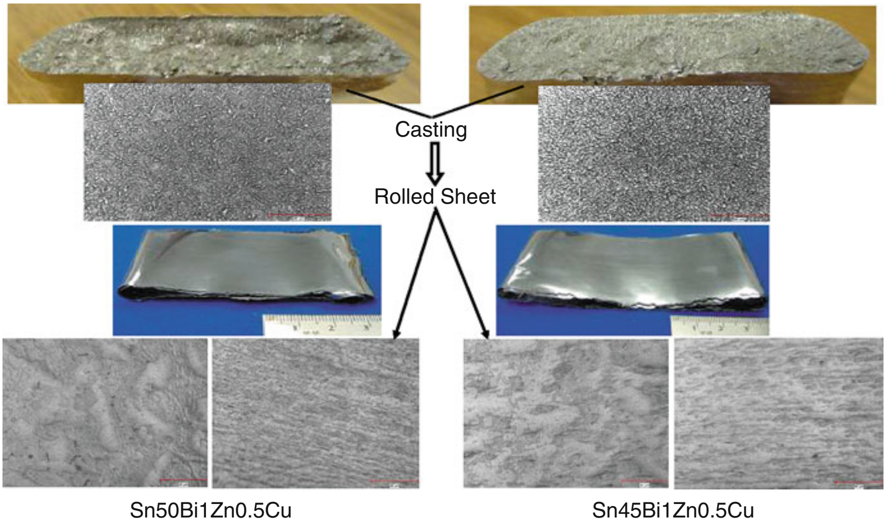


Fig. 8.12 Microstructure of casting and rolled Sn–Bi solders refined by Zn and Cu

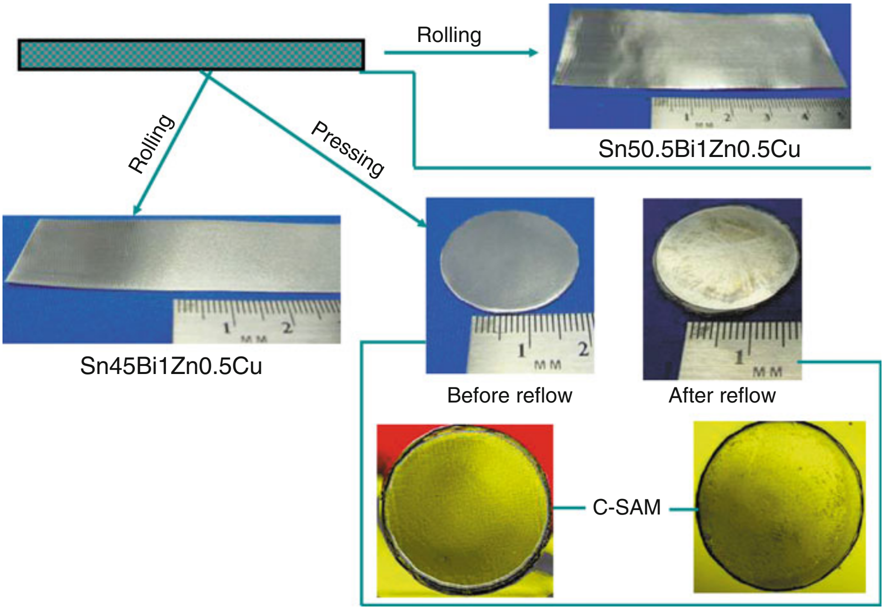


Fig. 8.13 Rolled/pressed ductile TIM1 preform/tape exhibited good manufacturability

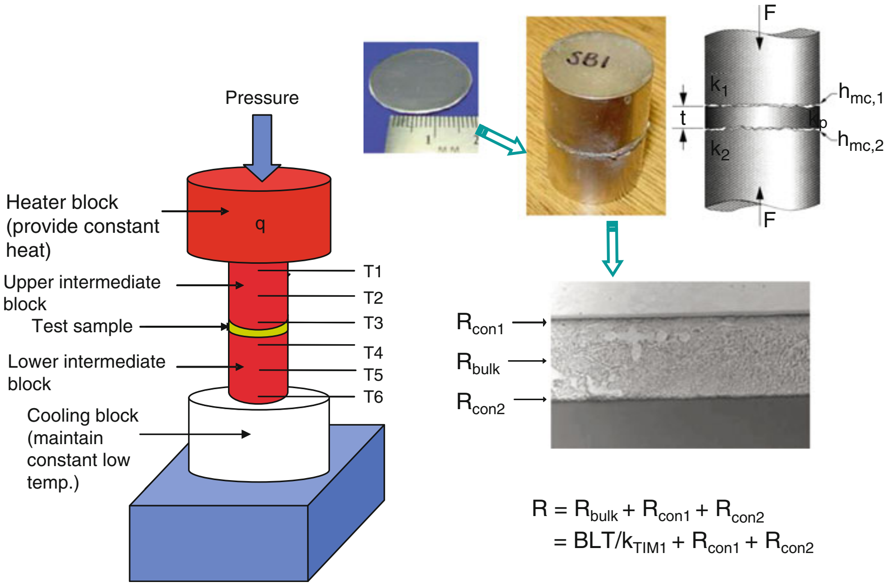


Fig. 8.14 Test method for thermal resistance that is the sum of the contact resistance and the bulk resistance of the TIM1

And the joint conductance is determined by

$$h_{\mathrm{j}} = \frac{1}{1/h_{\mathrm{c},1} + 1/h_{\mathrm{bulk}} + 1/h_{\mathrm{c},2}}. \tag{8.13}$$

The joint resistance is related to two regions: (1) microscopic interfacial region, where the contact resistance dominates the solder/substrate joint conductance. Good metallurgical bonding would eliminate or minimize the contact resistance, and make the contact resistance is much smaller than bulk resistance. (2) Bulk TIM1 region, where the bulk resistance of the TIM1 dominated by thermal reinforcement, such as Cu screen. The tested thermal resistance of typical hybrid metallic TIM is 0.015–0.025 °C cm^2/W, which is very competitive among the TIMs. Figures 8.15–8.19 show modeling, experimental example, and assessment result. Figure 8.20 provides possible processes to fabricate, apply, and attach the hybrid TIMs to electronic packaging assembly.

Gold–Gold Interconnection

Gold–gold interconnection (GGI) with gold stud have been developed as a niche segment of the flip chip bonding that emerges as one of the high growth areas of semiconduct assembly. GGI is a lead-free process where the Au bumps and

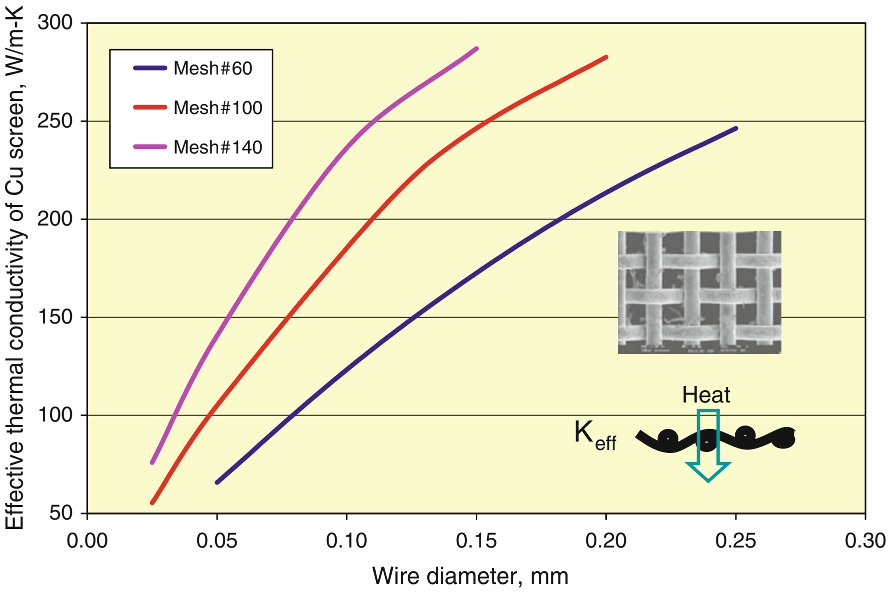


Fig. 8.15 Cu screen selection: Mesh#-Wire size-Thermal Conductivity-K_{eff} of Cu screen depends on wire and mesh number, assuming the wire is thermally isostatic

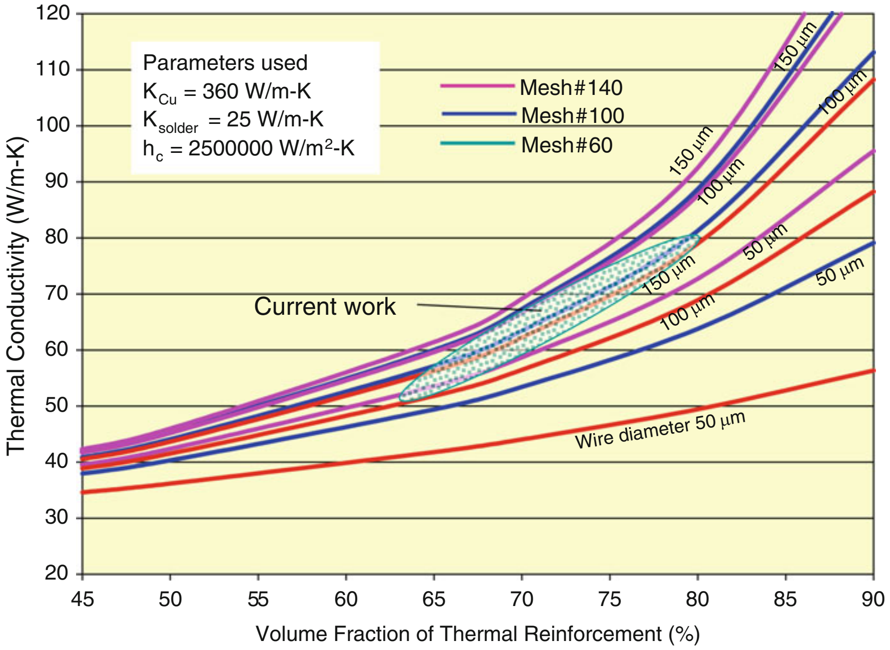


Fig. 8.16 Predicted thermal conductivity of TIM1 with increasing vol% of reinforcement

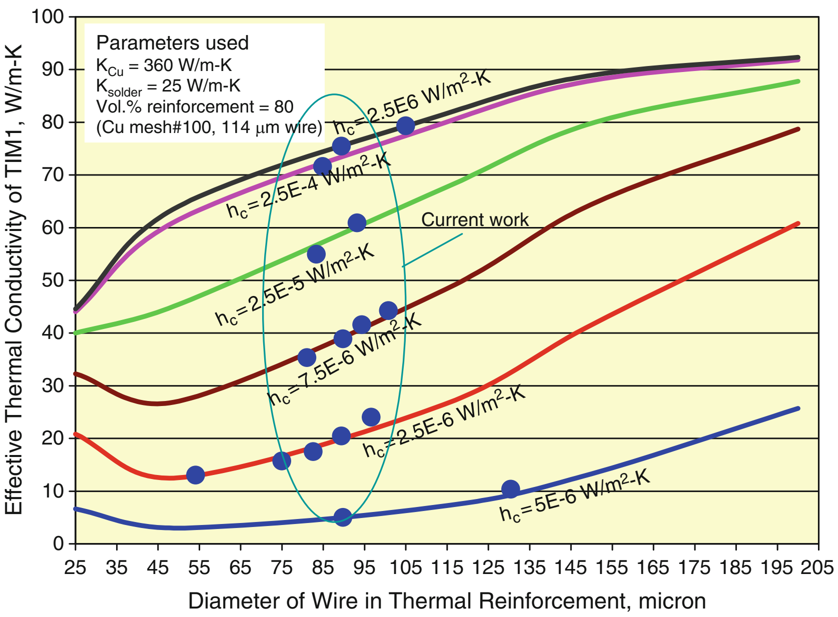


Fig. 8.17 How interface thermal barrier affect thermal conductivity of TIMI–good interface bonding is the key to enhance the thermal conductivity

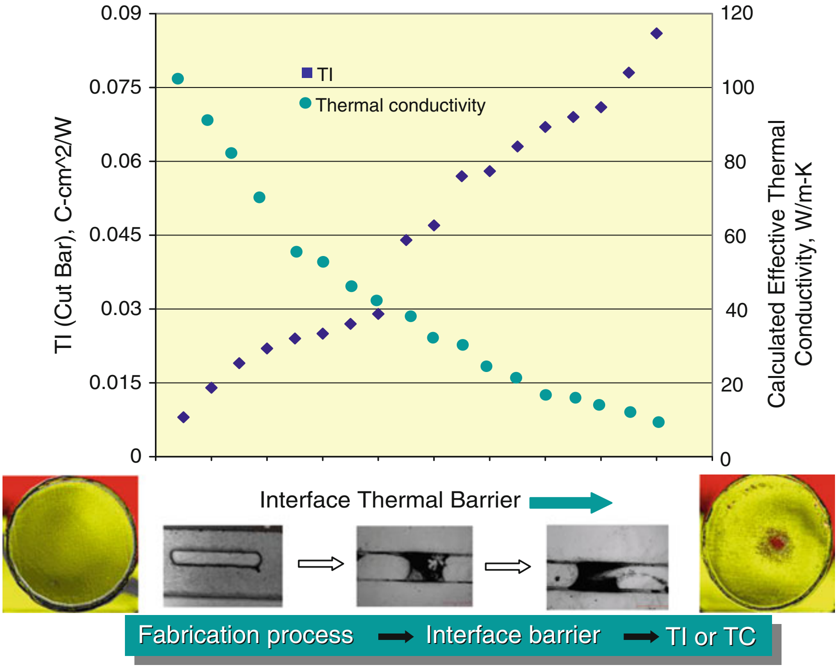


Fig. 8.18 Effect of interface barrier on thermal impedance (TI) and effective thermal conductivity of TIM1

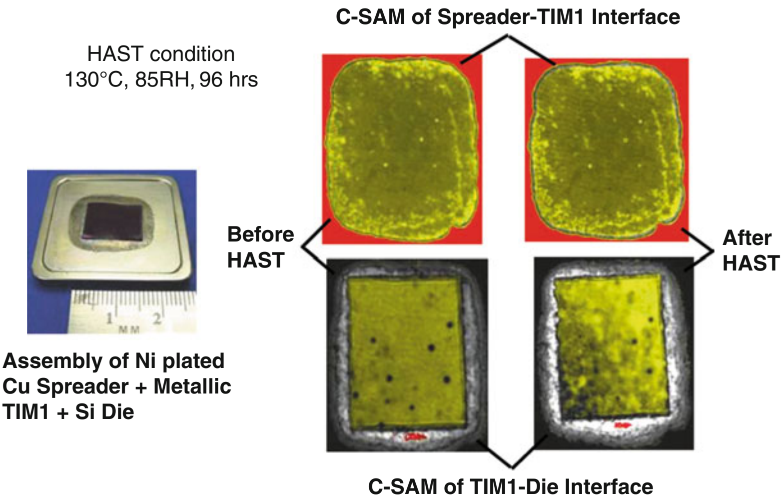
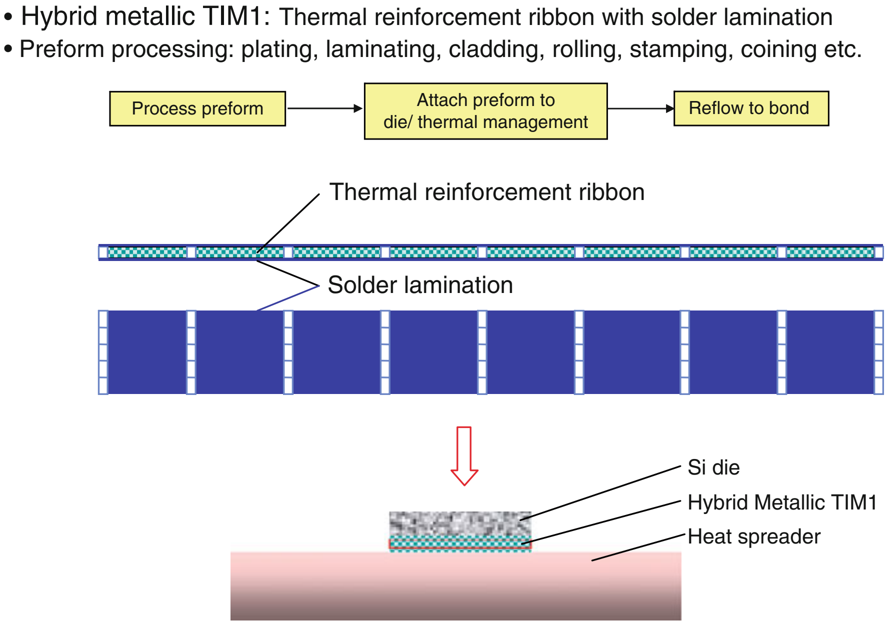


Fig. 8.19 Highly accelerated stress test (HAST)–no visual change from C-mode scanning acoustic microscope before and after HAST



- Hybrid metallic TIM1: Thermal reinforcement ribbon with solder lamination
- Preform processing: plating, laminating, cladding, rolling, stamping, coining etc.

Fig. 8.20 Application flow map–preform attachment

Au bond pads are joined together by heat and ultrasonic power under a pressure head. Gold bumping uses a variation of traditional wire bond technology to generate gold bumps on a wafer. After bumping, a wafer is diced and flipped, then thermosonically welded to the gold-plated substrate metallurgically, a monometallic thermosonic weld has higher strength and reliability than a solder joint produced by conventional flip chip methods. At the same time, the GGI joining also functions as an excellent TIM because the gold has a superior thermal conductivity of up to 318 W/m K, and the metallurgical bonding provides extremely small interface resistance. Furthermore, the use of a GGI flip chip assembly process will help to eliminate equipment parts and processing steps of the traditional flip chip assembly process and hence will shorten the overall cycle time. The materials characteristics of the GGI joining provide facet benefits. Gold resistivity is 80–85% lower than leaded and lead-free solder alloys, providing better current-carrying capacity. The thermal conductivity is much higher than solders, aiding head transfer and dissipation. Unlike solder bumped packaging, gold stud and GGI does not require under bump metallization or an interposer. When dice are small and the CTE is well matched to the substrate, GGI often does not require an under fill. Under fill is an expensive process required for solder flip chip, because solder is prone of fatigue fracture during thermal cycling. Gold stud bumping can produce small, inexpensive bumps at 50-μm fine pitch that are inherently taller than plated bumps. Plating processes have difficulty achieving this capability without additional expensive masking operations. Therefore, GGI joining can provide a highly thermally conductive interface infrastructure, it is not only a lower cost of ownership, but also demonstrates higher strength and conductance, and a greater flexibility than conventional flip chip methods.

The Gold–gold joining has been applied for high-brightness light-emitting diode (LED) construction, and complementary metal oxide semiconductor (CMOS) image sensors and other areas. Traditionally, LEDs used wire bond processes by changing to the flip chip GGI attachment method, high thermal conductivity, and low electrical resistance of the GGI are superior to solder bump flip chip. GGI flip chip bonding technology has been developed to bond the integrated circuit (IC) drive chip on the IC suspension used in hard disk drives. With the IC suspension design, it becomes possible to assemble the IC drive chip close next to the magnetoresistive head slider on the suspension (Luk et al. 2002).

Gold stud with conductive adhesive assembly is another emerging thermal interface infrastructure for flip chip interconnection. Originally found principally in low bump count and low-cost applications such as smart cards, adhesive assembly has now moved upscale to applications such as implanted medical devices and large imaging (infrared and X-ray/gamma-ray) detector arrays. While indisputably lead free, many other advantages of adhesive over solder bump flip chip assembly clearly foretell a wider role for adhesive flip chip assembly in tomorrow's demanding products. It is not only lead that vanishes with adhesive assembly. Because adhesives require no fluxing, the postcleaning required to remove flux residues also vanishes. The problems that flux residues cause in underfill delamination and in long-term reliability similarly vanish with the fluxes. Adhesive assemblies emerge from the curing oven ready for underfill, if required. The more compliant gold bumps and adhesive can tolerate higher thermal expansion differences between chip and substrate without underfill. Large arrayed silicon detectors with thousands of connections often do not require any underfill, since they are assembled to thermally matched silicon readout chips. Adhesives are suitable for extremely high density interconnects, presently dominated by indium bump bonding, also known as hybridization. Hybridization requires indium bumps on both mating surfaces, cold-welded by applying high pressure. Adhesive assembly arrays with bump pitches as low as 50 μm are much less costly than indium hybridization. Common adhesive cure temperatures of 150°C and below are far lower than today's eutectic solder, and far lower than candidate lead-free solders. For temperature-sensitive materials such as compound semiconductors or polymer-based devices such as pyroelectric detectors, adhesive cure temperatures may be less than 80°C. Special low curing temperature adhesive formulations allow room temperature curing when needed. Gold stud bumps commonly are combined with adhesive attachment. Although direct gold-to-gold interconnection, with no adhesive, is a reliable flip chip technique, the required high thermocompression forces limit it to lower bump counts. In contrast, gold stud bumps placed into conductive adhesive bumps require very low normal forces, making this method suitable for large chips with thousands of connections. Stud bumps can be placed directly on an IC's standard aluminum bond pads with no special preparation, although a light plasma cleaning may be used to remove any contamination on the pads. The costly and complicated multistep process of under bump metallization required for solder bumping is eliminated. Whole wafers, partial wafers, or even individual diced chips can be easily gold stud bumped, eliminating the dependency on processing full wafers which is typical of most solder bumping processes (Clayton 2005).

Adhesive attachment may relax the process window for coplanarity. The adhesive itself compensates for small variations in stud bump height. The adhesive also can be used to identify bumps that may be excessively low by visually inspecting for adequate epoxy transfer onto all bumps before curing the adhesive. If high pin count die makes sequential stud bumping of an entire wafer unacceptably slow, electroplated gold bumps offer an alternative. The main advantages of electroplated bumps are the bumping time per wafer, and a higher overall bump height if thick photoresist is used. The isotropic conductive adhesives (ICA) commonly combined with gold stud bumps are epoxies loaded with up to 80% silver flakes, ranging from 5 to 30 μm in diameter. The flakes tend to lie atop one another like a pile of wet leaves. Cured ICA has the same electrical conductivity in all directions (isotropic). More expensive gold, palladium, or platinum flakes are used in those applications, such as implanted medical devices, which are not compatible with silver. Carbon nanotubes (CNTs) currently are being tested as a potential alternative to silver flakes, although at present, they are rather expensive. In addition, nanotubes have a strong tendency to agglomerate, preventing a uniform distribution of the conductors when mixed into a resin matrix. In summary, the emerging trend toward a gold-bump/adhesive system brings with it a demonstrated, well-tested solution for low-temperature, flux free, lead-free, flip chip assembly. However, beyond those obvious advantages, the low-temperature assembly and manufacturing flexibility

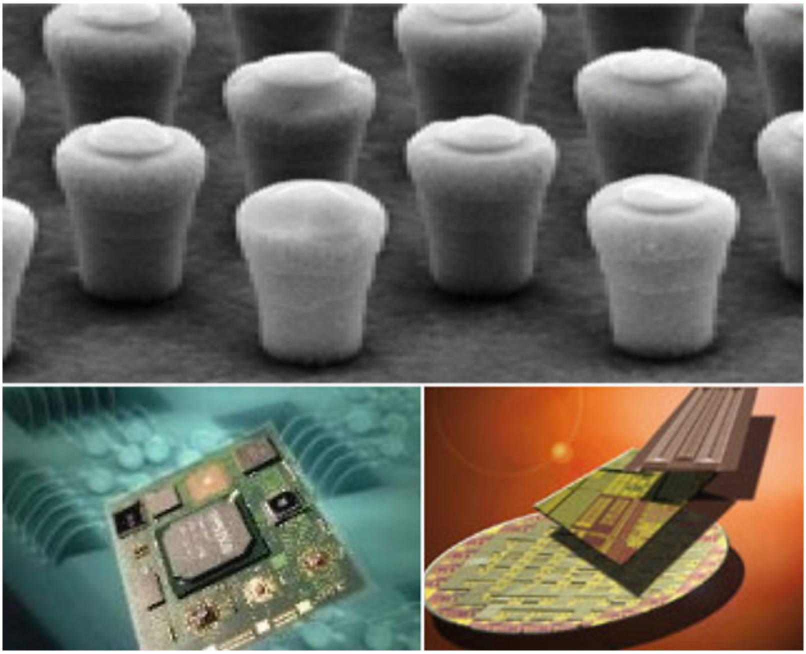


Fig. 8.21 Gold nanolawn for electronic interconnection (Bock 2009)

of gold bump adhesive assembly link it closely to the latest trends in semiconductor and sensor device development. Looking toward a future world of plastic ICs, polymer memory chips, and a variety of sensors fashioned from compound semiconductors, gold bump conductive adhesive may become the only practical, economical choice for low temperature flip chip assembly (Clayton 2005).

Gold nanolawn is a completely new interconnection technique, as shown in Figure 8.21, which promises substantially higher integration densities using techniques such as flip chip. The nanolawn is produced by means of nanoscaled lithography, through-mask electroplating on bond pads, and cold welding. Daisy chains and Kelvin structures were used to characterize the interconnections electrically. The results showed that the resistance of a single 25 × 25 μm connection is about 1 mΩ. Daisy chains with 360 elements confirmed high reliability and excellent electrical properties (Bock 2009).

Organic Thermal Interface Materials

If the metallic TIMs are mainly suitable to TIM1 applications, organic TIMs would mostly be used for TIM2 application, although some metallic or organic TIMs have been developed for both TIM1 and TIM2 applications (Mahajan et al. 2002). With advances in packaging technology, the proper selection of a TIM has become more complicated as each application will have different design requirements. The final selection will encompass material properties and process considerations beyond the thermal performance of the material. Compliance, thickness, processing, and response to reliability conditioning are key considerations when engineering the final package. To conform the diversified requirements of advanced processor and packaging technology, different formats of organic TIM have been developed and commercialized such as various thermally conductive elastomers, thermal greases, PCM, and PSH materials. Despite the maturity of the organic TIM market, there continues to be a need for higher performance and value-added materials. The performance requirement for a TIM encompasses more than thermal performance but a total solution: low thermal resistance across a bond line, high thermal conductivity, reworkability, sufficient thickness to accommodate nonplanarity, compliance for thermal mismatch, preapplication to heat spreader (TIM1) or a heat sink (TIM2) for speed of assembly, and low cost. For instance, both grease and PCMs possess low thermal resistance due to their liquid nature at operating temperature and thin bond line, however, each possess drawbacks. The reliability and messy nature of grease is a concern, whereas the reworkability and low thermal conductivity for PCMs are drawbacks. Pad and film formats offer many advantages from a processing and packaging perspective, but traditionally, their performance is not as high as grease or PCM. There exists a strong need for high-performance organic TIMs as the strength of those TIMs makes them useful for both TIM2 and TIM1 applications. The emerging high performance organic TIMs include PSH and advanced thermally conductive elastomers. This section will give a review on the status and future trend of various organic TIMs.

Thermally Conductive Elastomer Materials

Thermally conductive elastomers are elastomeric materials which contain a thermally conductive fillers. Depending on loaded fillers, the thermally conductive elastomers can mainly be classified into insulated TIM and noninsulated TIM. Insulated TIM is usually loaded with thermally conductive ceramic fillers. They are primarily used in electronics applications in instances where good thermal conduction and electrical insulation are needed in the same material. For example, when the material is used as TIM2, thermally conductive elastomer material is used as a thermally conductive, electrically insulating interface between the electronic component and the metal heat sinks. Because of their high electrical conductivity, metal heat sinks cannot be in direct contact with electronic components. The thermal conductivity of thermally conductive elastomers is generally much less than that of the metal heat sink. Thus, the thermal conductivity of the thermally conductive elastomer limits the overall ability of heat dissipation.

Noninsulated TIMs are loaded with high thermal conductivity metallic or graphite fillers and aim to replace some solders for electronic assembly. These metal-loaded elastomers pay a penalty in viscosity and adhesive quality to incorporate the higher conductivity materials. As discussed previously, efforts to create high conductivity metallic TIMs have been progressing with some success. These metallic TIMs require fundamentally different application processes and can sometimes strain thermal budgets for the attached devices. As a result, there is still a vigorous effort to improve the filled polymer systems (Mahajan et al. 2002).

Typical thermally conductive elastomer contains ceramic filler such as BN or alumina in an elastomer matrix. The elastomers used are usually urethane or silicone based. While these materials are adequate in many instances, there is a constant demand for thermally conductive elastomers with improved thermal conductivity and electrical insulating properties. For electrical insulating TIM, the thermally conductive electrical insulating filler may be any conventional filler such as boron nitride, alumina, magnesia, or aluminum nitride. Hexagonal BN is the preferred filler. The proportion of filler in the composition is preferably about 45–70 vol%. For BN fillers, the filler preferably forms about 65–80 wt% of the composition. Any conventional particle size may be used. Preferably, the filler particle size is about 5–200 μm, and the filler will contain a mixture of coarse (100–200 μm) and fine (10–50 μm) particle sizes. High bulk density fillers generally provide better thermal conductivity. For alumina fillers, any conventional α-alumina can be used, however, tabular alumina is preferred. The elastomer may be any thermoplastic elastomer, preferably a block copolymer. Preferred block copolymers are styrenic copolymers and olefin copolymers. Particularly preferred are styrene-ethylene-butylenestyrene block copolymers. Examples of these block copolymer elastomers are Kraton® G-1652-M and Kraton® G-657-MX sold by the Shell Chemical Co. These Kraton® elastomers have styrene/rubber ratios of 29/71 and 13/87, respectively. If desired, a cross-linkable elastomer such as Shell Chemical's Kraton® 1901-X or RP-6501 may be used as the elastomer. Cross-linkable elastomers have functional groups such as carboxyl groups or ethoxy silanol groups which are reacted to cross link the elastomer molecules. Any suitable cross-linking agent and a cross-linking catalyst may be combined with the cross-linkable elastomer to bring about the cross linking. Cymel® 303 (hexamethoxymethylmelamine) sold by American Cyanamid Co., is a preferred cross-linking agent for Kraton® 1901-X; Cycat® 600 (aromatic sulfonic acid) sold by American Cyanamid Co., is a preferred cross-linking catalyst for Kraton® 1901-X; Dibutyl tin dilaurate is a preferred cross-linking catalyst for Kraton® RP-6501. The relative proportions of cross-linkable elastomer, cross-linking agent, and cross-linking catalyst may vary depending on the compounds used and the degree of cross linking desired. For hexagonal BN fillers, the filled elastomers preferably have a thermal conductivity of at least about 12×10^{-3} cal/s cm K, more preferably at least about 15×10^{-3} cal/s cm K. The filled elastomers may be made in any conventional form such as blocks, sheets, or films using any conventional method. A preferred method for making the filled elastomers employs a solvent-containing precursor composition. The elastomer is dissolved in an appropriate solvent to form a solution. The amount of solvent can be any amount which effectively dissolves all the elastomer. Typically, the solvent forms about 50–85 wt% of the elastomer-solvent solution. The thermally conductive filler is then added to form the precursor composition. The composition is dried to remove the solvent. The composition is shaped before and/or after the drying step. Before drying, the composition may be cast in a mold or as a film or sheet. After drying, the composition is pressed at elevated temperatures. The drying temperature may vary depending on the solvent and elastomer involved as well as the drying time. The drying is performed for about an hour at about 70–120°C. The pressing is performed at 500–10,000 psi, more preferably about 1,500 psi. The pressing temperature is about 150–175°C. If a cross-linkable elastomer is used, a cross-linking agent and catalyst would be added to the precursor mixture. The solvent may be any suitable solvent. Toluene is a preferred solvent. The amount of solvent used is the minimum needed to form a workable precursor composition (Block et al. 1993).

The typical format of thermally conductive elastomers are silicone elastomer pads filled with thermally conductive ceramic particles, often reinforced with woven glass fiber or dielectric film for added strength. These elastomers are available in thickness from about 0.1–5 mm and hardness from 5 to 85 Shore A. Unlike compounds and greases, elastomer pads provide electrical insulation and can be used between surfaces that are at different electrical potential. They are typically used under discrete power devices where electrical isolation is required.

Elastomers do not flow freely like greases or compounds, but will deform if sufficient compressive load is applied to conform to surface irregularities. At low pressures, the elastomer cannot fill the voids between the surfaces and the thermal interface resistance is high. For example, when the thermal conductivity of highly conductive elastomer reaches 5 W/m K ($R_{c\text{-}s}$ is 1.8 °C/W), twice that of grease, inspection of the disassembled interface after the test showed that there was less than 30% contact between the material and the two surfaces. As pressure is increased, more of the microscopic voids are filled by the elastomer and the thermal resistance decreases. For most high durometer materials, mounting pressures around 300–500 psi eliminate the interstitial voids and reduce interface resistance to a minimum. Mounting pressure must be permanently maintained by using fasteners or springs to hold the two surfaces together (deSorgo 1996).

As one of elastermic noninsulating TIMs, thermally conductive adhesive tapes are double-sided pressure sensitive adhesive films filled with sufficient ceramic powder to balance their thermal and adhesive properties. The adhesive tape is usually supported either with an aluminum foil or a polyimide film for strength and ease of handling. Polyimide support also provides electrical insulation. Adhesive tapes perform much like the elastomeric films in that they also require some initial mating pressure to conform to irregularities in the mating surfaces. They are also unable to fill large gaps between nonflat surfaces. However, once the joint is formed, the adhesive tapes require no mechanical support to maintain the mechanical or thermal integrity of the interface. Adhesive tapes provide convenience in attaching a heat sink to a semiconductor package because, unlike liquid adhesives, no cure time is required. The film is applied to one of the surfaces, usually to the heat sink, and it is then forced into contact with the semiconductor package to complete the thermal joint. The application pressure is typically 10–50 psi for a few seconds' duration. The bond thus formed can be considered permanent and the heat sink is reliably attached to the semiconductor.

However, this convenience comes at a price. $R_{c\text{-}s}$ for tapes is only slightly better than a dry joint. This is because the thermal tapes do not fill gaps as well as liquids, and thermal joints made with tapes will normally include considerable interstitial air gaps. For the most part, the quality of the two joining surfaces will determine the amount of contact that can be achieved and the thermal performance that can be expected. The high shear strength of these thermal tapes means that reliable joints between heat sinks and semiconductors can be achieved, even with poor surfaces and no mechanical fasteners (deSorgo 1996).

Comparably, conductive elastomeric thermal interface pads can be compressed between the heat generator and the heat receiver. Pads are either electrically conductive or nonconductive, based on application. Pads are generally thicker than tapes and adhesives because the added thickness helps to fill larger gaps.

Thermal Grease and Compound

Thermal conductive greases, usually with a form of paste, are typically made up of silicone or hydrocarbon oils with a heavily loaded suspension of thermally conductive ceramic or metal fillers. The emulsion fillers increase thermal capacity and provide body to minimize flow out of the interface. The actual bulk thermal conductivity of the resulting material is low; however, because the paste-like consistency of the thermal grease allows the final bond line thickness to be very thin, the resulting thermal resistance across the interface can be quite low. As a two-part suspension, thermal greases can separate to form voids and dry out over time, especially in service with high temperatures or extensive thermal cycling. Therefore, the paste-like nature can lead to inconsistent and messy application issuers (deSorgo 1996).

Sufficient grease is applied to one of the mating surfaces such that when pressed against the other surface, the grease flows into all voids to eliminate the interstitial air. Excess grease flows out past the edges and the thinnest possible thermal joint is formed as the two surfaces come into contact at their high points. Joint integrity must be maintained with spring clips or mounting hardware.

Thermal greases are notoriously user unfriendly, but provide very low thermal resistance between reasonably flat surfaces. Grease does not provide electrical insulation between the two surfaces, and excess grease that flows from the joint should be cleaned up to prevent contamination problems. Greased joints can also dry out with time, resulting in increased thermal resistance. The effect of thermal grease and other TIMs on heat transfer through an interface can be seen in Table 8.5. These data were generated using a P54C Pentium Thermal Test Die powered to 6 W in an AMP Socket 5. A Wakefield 799–80 AB pin fin heat sink was attached with a spring clip. Without an interface material, $R_{c\text{-}s}$ was 2.9°C/W. The addition of thermal grease to the joint reduced the resistance to 0.9°C/W. Inspection of the joint after testing showed that the grease covered over 90% of the area and the thickness was less than 0.07 mm (deSorgo 1996).

Table 8.5 Case-sink and junction ambient thermal resistance for various interface materials (deSorgo 1996)

Thermal interface joint	Thickness in/mm	Thermal conductivity (W/m K)	Thermal resistance $R_{c\text{-}s}$ (°C/W)	Thermal resistance $R_{j\text{-}a}$ (°C/W)
Dry joint	N/A	N/A	2.9	9.9
Thermal grease	0.003/0.076	0.7	0.9	8.1
Thermal compound	0.005/0.127	1.2	0.8	7.9
Conductive elastomer	0.01/0.254	5.0	1.8	8.9
Adhesive film	0.009/0.229	0.7	2.7	9.6

Thermally conductive compounds are an improvement on thermal grease as these compounds are converted to a cured rubber film after application at the thermal interface. Initially, these compounds flow as freely as grease to eliminate the air voids and reduce the thermal resistance of the interface. After the interface is formed, the compounds cure with heat to a rubbery state and also develop secondary properties such as adhesion. Formulations with adhesive properties do not require mechanical fasteners to maintain the integrity of the joint. Because the binder cures to a rubber, these compounds do not have the migration or the dry joint problems associated with thermal greases. Compounds can be used to fill large gaps where greases would bleed from the joint on account of their migratory nature. Clean up is also simple as excess material is easily removed after it has been cured to a rubber. The thermal performance of a typical compound is shown in Table 8.5. Because the compound behaves like a grease, the joint is nearly void free and the improvement in thermal resistance over a dry joint is similar to that of grease, 0.8 vs. 2.9°C/W (deSorgo 1996).

In addition, thermal conductive gels are similar to thermal grease with a new difference. The gel material is cured to form cross-linked polymer chains which provides lateral stability to minimize the problem associated with liquid TIM materials. Gels are reusable, however, they generally have a slightly lower thermal conductivity than thermal grease.

Phase Change Materials

PCM is a substance with a high heat of fusion and capable of absorbing and releasing heat when the material changes from solid to liquid and vice versa. In fact, latent heat storage of PCMs can be achieved through solid–solid, solid–liquid, solid–gas and liquid–gas phase change. However, the only phase change used for PCMs is the solid–liquid change. Liquid–gas phase changes are not practical for use as thermal storage due to the large volumes or high pressures required to store the materials when in their gas phase. Liquid–gas transitions do have a higher heat of transformation than solid–liquid transitions. Solid–solid phase changes are typically very slow and have a rather low heat of transformation (Wikipedia 2008).

When PCMs reach the melting temperature at which they change phase, they absorb large amounts of heat at an almost constant temperature. The PCM continues to absorb heat without a significant raise in temperature until all the material is transformed to the liquid phase. When the ambient temperature around a liquid material falls, the PCM solidifies, releasing its stored latent heat. A large number of PCMs are available in any required temperature range from -5 up to 190°C. Typical PCMs include organic [paraffin (C_nH_{2n+2}) and fatty acids ($CH_3(CH_2)_{2n}COOH$)], inorganic [salt hydrates (M_nH_2O) and eutectic materials (organic–organic, organic–inorganic, inorganic–inorganic compounds). The advantages of organic PCMs include availability in a large temperature range, freezing without much super cooling, ability to melt congruently, self nucleating properties, compatibility with conventional material of construction, no segregation, chemical stability, high heat of fusion, safe and nonreactive, and recyclable. Their major disadvantages are low thermal conductivity in their solid state, high heat transfer rates are required during the freezing cycle, volumetric latent heat storage capacity is low, and they are flammable. Due to cost considerations, only technical grade paraffins may be used which are essentially a paraffin mixture and are completely refined of oil (Wikipedia 2008).

The characteristics of inorganic salt hydrates (M_nH_2O): high volumetric latent heat storage capacity, low cost and easy availability, sharp melting point, high thermal conductivity, high heat of fusion, low volume change, nonflammable, change of volume is very high, super cooling, and nucleating agents are needed and they often become inoperative after repeated cycling.

Eutectics have a sharp melting point similar to pure substance. Volumetric storage density is slightly above organic compounds. Only limited data are available on thermophysical properties as the use of these materials are very new to thermal storage application.

Thermal-composites have been developed by combinations of PCMs and other (usually solid) structures. A simple example is a copper mesh immersed in a paraffin wax. The copper mesh within paraffin wax can be considered a composite material, dubbed a thermal-composite. Such hybrid materials are created to achieve specific overall or bulk properties. Thermal conductivity is a common property which is targeted for maximization by creating thermal composites. In this case the basic idea is to increase thermal conductivity by adding a highly conducting solid (such as the copper-mesh) into the relatively low conducting PCM thus increasing overall or bulk (thermal) conductivity. If the PCM is required to flow, the solid must be porous, such as a mesh. Solid composites such as fiberglass or kevlar-pre-preg for the aerospace industry usually refer to a fiber (the kevlar or the glass) and a matrix (the glue which solidifies to hold fibers and provide compressive strength). A thermal composite is not so clearly defined, but could similarly refer to a matrix (solid) and the PCM which is of course usually liquid and/or solid depending on conditions (Wikipedia 2008).

In order to use for TIMs in electronic packaging, the PCM should possess:

1. Thermodynamic properties
   (a) Melting temperature in the desired operating temperature range
   (b) High latent heat of fusion per unit volume
   (c) High specific heat, relatively high density and high thermal conductivity
   (d) Small volume changes on phase transformation and small vapor pressure at operating temperatures to reduce the containment problem
   (e) Congruent melting
2. Kinetic properties
   (a) High nucleation rate to avoid super cooling of the liquid phase
   (b) High rate of crystal growth, so that the system can meet demands of heat recovery from the storage system
3. Chemical properties
   (a) Chemical stability
   (b) Complete reversible freeze/melt cycle
   (c) No degradation after a large number of freeze/melt cycle
   (d) Noncorrosive, nontoxic, nonflammable, and nonexplosive materials
4. Economic properties
   (a) Low cost
   (b) Large-scale availabilities

Based on this baseline, some special form of phase change TIMs have been developed for electronic packaging applications. The solid–liquid phase change is used for TIMs because a liquid is associated with high conformability, which is needed for minimizing interfacial air pockets, thereby reducing interface thermal resistance. The PCM should melt at a temperature slightly above room temperature (e.g., 45°C) so that the material is a liquid while it functions as a TIM. The liquid is attractive in that it is conformable, but it is disadvantageous in the possibility of seepage and consequent contamination of the surrounding electronic components. By having the interface material be a solid during operation of the electronics at temperatures below the melting temperature, the seepage problem is alleviated. Furthermore, the absorption of the latent heat of fusion during melting provides an additional mechanism of heat dissipation. Both the organic (such as paraffin wax) and inorganic ones (most commonly metal salt hydrates, e.g., disodium hydrogen phosphate dodecahydrate) can be used for TIMs. The organic materials are attractive in their low reactivity, stability in the phase change characteristics under thermal cycling and low supercooling, but they tend to be poor in thermal conductivity. The inorganic materials are attractive in their relatively high thermal conductivity, but they suffer from relatively high reactivity, high supercooling, and poor stability in the phase change characteristics under thermal cycling. For application as TIMs, the organic PCMs are preferred, such as paraffin wax or silicon-based TIMs. The thermal conductivity of a PCM can be increased by using a filler (particles, fibers, or bars) that is thermally conductive. The filler does not melt, but its presence can affect the phase change characteristics, including the melting temperature and the heat of fusion. Due to the low thermal conductivity of the organic PCMs, the use of thermally conductive filler is important. An alternate method of increasing the thermal conductivity involves impregnating porous graphite with paraffin wax, but this method suffers from the inability of the resulting composite to conform to the topography of the surface from which it is to absorb heat. Furthermore, the volume fraction of the component that undergoes phase change is limited. The choice of the organic matrix of a PCM for use as a TIM depends on the melting temperature, the conformability in the molten state, the extent of undercooling during solidification, the latent heat of fusion, and the ability to withstand elevated temperatures. The conformability strongly affects the effectiveness as a TIM, but it is an attribute that is difficult to measure. For instance, carbon black can be a secondary filler used in the TIM because of its exceptional conformability, which is a consequence of its being in the form of porous agglomerates of nanoparticles. Due to its conformability, carbon black is even more effective as a filler in thermal pastes than highly conductive fillers when the mating surfaces are sufficiently smooth (such as 0.05 μm).

A polycaprolactone diol (molecular weight = 2,000 amu) filled with hexagonal BN particles (4 vol%) is an effective phase-change TIM. It exhibits a melting onset temperature of 37°C and a solidification onset temperature of 34°C. The thermal contact conductance across copper mating surfaces (15 μm roughness) is 8×10^4 W/m^2 °C at 70°C and a pressure of 0.69 MPa. The combination of high conductance and high resistance to elevated temperatures makes this material superior as a phase-change TIM to BN-filled paraffin wax, polyvinyl ether, polytetramethylene ether glycol, tetradecanol, lauric acid, polyester diol, polyester triol, or polycaprolactone diol (molecular weight = 1,000 amu). However, the heat of fusion is lower for the polyols than many other organic materials. The conductance attained by BN-filled diols is higher than that attained by commercial phase-change TIMs. BN is more effective as a filler than carbon black for providing high conductance, but carbon black reduces the heat of fusion by a smaller amount than BN does (Liu and Chung 2006).

While novel PCMs are continuously emerging, commercial PCMs provide a combination of grease-like thermal performance with pad-like handling and installation convenience. They have compositions that transform from a solid at room temperature to a mixture of solid and liquid phases at various operating temperatures. The liquid from the mixture makes intimate contact with the contact surfaces while the solid retains the integrity of the gap. At this operating temperature, the PCM is able to act like thermal grease, allowing it to form a thin bond line. Sometimes the installation process requires some compressive force to bring the two surfaces together and cause the material to flow until the two surfaces come into contact at a minimum three points, or the joint becomes so thin that the viscosity of the material prevents further flow. Excess liquid should then flow to the perimeter of the interface and solidify so it remains away from the other components. Solid at room temperature, PCMs are melted (i.e., undergo a phase change) as the temperature rises to the 40–70°C range. This makes the material (0.13 mm thick in its dry film form) as easy to handle as a pad, while assuring that it will, when subjected to heat during the assembly process, flow into voids between mating surfaces as effectively as thermal grease. Ordinarily, applying power to the electronic component introduces the needed heat for the phase change to occur, establishing a stable thermal joint. These materials consist of organic binders (i.e., a polymer and a low-melt-point crystalline component, such as a wax), thermally conductive ceramic fillers, and, if necessary, a supporting substrate, such as aluminum foil or woven glass mesh (deSorgo 1996).

Typical phase-change TIMs have the following characteristics:

(1) Compressible phase-change interface materials that compensates for large area and extreme height tolerances and gaps.
(2) In situ curing thermal interface adhesive materials that provides up to 300 psi as applied and cure to over 600–1,200 psi over time at operating temperatures of the device.
(3) Available as electrically conductive or electrically insulating thermal adhesives, thermal greases, thermal gels, and thermal pads.
(4) Available as dry, single-sided, or double-sided pressure sensitive tacky thermal interface pads and thermal adhesives film tapes.
(5) Available in preforms of thermal PCM pads and thermal adhesive films and tapes.
(6) Phase-change thermal interface pad materials that flow at 55, 90, 130, and 180°C respectively.
(7) PCM of all thickness with outstanding thermal conductivitity and low thermal interface resistance to help cool and manage power devices as adhesives, greases, gels, and gap filling compressible thermal pads.

In summary, PCMs provide a combination of grease-like thermal performance with pad-like handling and installation convenience. They have compositions that transform from a solid at room temperature to a mixture of solid and liquid phases at various operating temperatures. The liquid from the mixture makes intimate contact with the contact surfaces while the solid retains the integrity of the gap. At this operating temperature, the PCM is able to act like thermal grease, allowing it to form a thin bond line. Sometimes the installation process requires some compressive force to bring the two surfaces together and cause the material to flow, until the two surfaces come into contact at a minimum three points, or the joint becomes so thin that the viscosity of the material prevents further flow. Excess liquid should then flow to the perimeter of the interface and solidify so it remains away from other components.

Polymer Solder Hybrid Materials

As one special form of the PCMs, PSHs provide superior long-term reliability performance, and exhibit the lowest thermal impedance of the phase-change family. For optimum performance, the material must be exposed to temperatures above the melting point of contained solder(s) during operation or by a burn-in cycle to achieve lowest thermal impedance and highest thermal performance. Upon reaching the required burn in temperature, the material will fully change phase and attain minimum bond-line thickness less than 0.001 in. or 0.0254 mm and maximum surface wetting. They are typically used in microprocessors, graphics processors, chipsets, memory modules, power modules, and power semiconductors. Material may flow when oriented vertically, especially at higher temperatures. This does not affect thermal performance, but should be considered if appearance is important (Chomerics 2009).

Conventionally, as shown in Figure 8.22, PSHs comprise a siloxane-based polymer and a solder such as indium–silver, indium–tin, tin–bismuth, gallium–tin–indium, gallium–indium–tin–zinc, indium–bismuth, gold–tin or other solder material. Additionally, thermally conductive fillers such as aluminum, silver, copper, or graphite may also be added to the PSH TIM. The combination of conductive filler and solder allows for the formation of thermally conductive pathways or chains throughout the PSH TIM. In this manner, heat generated within the die may be readily transferable across such chains to the attached thermal management device for heat dissipation.

In order to form the indicated chains and properly secure the thermal management device to the die, the PSH TIM is heated by a reflow process to at least the melting point of the solder. 183°C is considered the industry standard dividing line between "low melt" and "high melt" solders. Where conventional solders, such as those mentioned above, are used, the PSH TIM may be a high melt solder requiring reflow at temperatures in excess of about 260°C, for the solder to melt and allow the filler to diffuse there into. For example, a temperature of 260°C may be required where a gold–tin solder is used in the PSH TIM. However, even where other

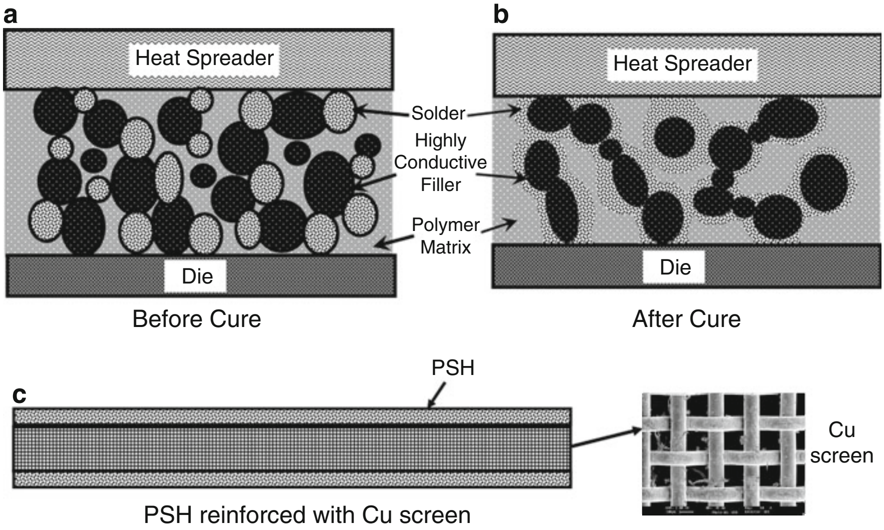


Fig. 8.22 Illustration of polymer solder hybrid (PSH) thermal interface material (**a**) Before cure; (**b**) After cure, a continuous highly conductive network is formed in the polymer matrix for heat conduction, benefiting of solder conductivity without the compliance issues; (**c**) The thermal conductivity of PSH can be enhanced with Cu screen

conventional solders are used, it is not uncommon for a temperature in excess of about 183°C to be employed.

For TIM1 application, the design target for the PSH performance requirement usually includes: (1) Thermal resistance of the PSH between values of indium and grease: TI $<$ 0.10 C cm^2/W, preferably $<$0.05 °C cm^2/W at BLT 2 mil. (2) Dispensable paste format-syringe dispensable. (3) Pot life $>$ 8 h (full shift). (4) Reliability to meet or exceed industry standards–thermal cycling, HAST, high temperature aging. (5) Solder partially melts at less than 100°C for self healing of microcracks at device operating temperature, and for increasing conductivity at hotspots. A PSH TIM may be used to secure a thermal management device to a temperature-sensitive assembly. For example, larger mobile or bare die assemblies incorporated into an already assembled computing box, such as a laptop, may require use of a PSH TIM. Such assemblies may include a die requiring attachment of a heat management device such as a heat pipe. These assemblies include more than just a die or individual semiconductor package. Rather, these assemblies are closer to being a completed computer, such as the indicated laptop, with added temperature sensitive features.

For temperature-sensitive assemblies, low melt solders are available having melting points lower than about 183°C. However, a PSH to serve as a TIM that employs a low melt solder tends to be highly susceptible to degradation when subjected to standard industry testing. Industry tests may include a HAST which includes PSH exposure to more than 100°C (e.g., about 130°C) with relative humidity of more than 50% (e.g., about 85%) for an excess of about 75 h (e.g., about 100 h), or a standard bake test which includes PSH exposure to even higher temperature (e.g., 150°C for about 100 h) without degradation. Unfortunately, a PSH employing a low melt solder tends to degrade in between about 24 and 48 h when subjected to such tests (Koning and Hua 2004).

While a low melt solder, such as indium–tin–bismuth, would normally degrade or lack the robustness necessary to remain intact when subjected to a HAST, the addition of some fillers prevents such an occurrence. These fillers include finely distributed copper, gold, or silver particles or copper-, gold-, or silver-coated particles. The fillers provide a sufficient degree of robustness to the PSH TIM following reflow, such that the PSH TIM remains intact following exposure to conditions such as HAST conditions (Koning and Hua 2004).

The polymer matrix may be a material that can be applied as a paste such as a dispensable syringe or by screen printing. The polymer matrix may also act as an adhesive to bond the two mating parts together. The nonfusible particles, such as most metals, benefit from a high thermal conductivity, however, a thermal flow path through the TIM is limited by the point-to-point contact of the particles as shown in Figure 8.22. Nonfusible particles refer to particles that will not melt and flow during packaging assembly process, reliability testing, and product operation and so remain as point contacts with each other. This provides thermal conductivity through the TIM that is limited to point-to-point percolation, resulting in a thermal bottleneck through the nonfusible particles (Jayaraman et al. 2007).

The phenomenon of percolation describes the effects of interconnections present in a random system, here the number of filler particles that are randomly in point contact with each other to allow thermal conduction. Normally, to improve conduction limited by percolation, the amount of filler could be increased until a threshold amount is reached and heat conduction, due to the filler, transitions to a sufficiently high value. The volume fraction of filler required to reach this transition level may be too high and can overpower the properties desired from the polymer binder such as low-contact resistance. Another problem is that for some metal particles in contact with some polymer binders, the bare particle filler can poison the polymer cure such as by hindering or blocking the curing agent (Koning et al. 2006).

To address these concerns, a PSH TIM has been developed that includes fusible particles as well as filler particles in a silicone polymer matrix material. The fusible particles melt during the assembly process and can therefore wet the filler particles or self coalesce. Thereby the average particle size grows creating long continuous heat transfer pathways that alleviate the thermal bottleneck of percolation. The fusible particles, e.g., solder material, may be materials such as solder-like materials that melt below approximately 300°C. Solder materials include pure metals, such as indium and tin, alloys of several metals such as In, Cu, Ag, Sn, Bi, Pb, Cd, Zn, Ga, In, Te, Hg, Tl, Sb, Se, Po, or mixtures of any two or more thereof, or another metal or alloy having a melting point lower than that of the metal powder in component. The filler particles may be nonfusible materials with melting points well above 300°C, such as aluminum at 660°C, silver at 961°C, copper at 1,084°C, gold at 1,064°C, etc. Figure 8.22c shows that copper (Cu) mesh can be a effective high thermal conductivity reinforcement for PSHs with very thin BLT PSHs on either side of the copper mesh, providing excellent thermal conductivity and extremely low thermal resistance (0.05°C cm^2/W or below). In addition, Cu mesh can be a carrier for creating extremely thin BLT PSHs.

Silicone exhibits certain characteristics (e.g., low glass transition temperature and low moisture absorbency) that make it suitable as a binder matrix for PSH TIMs. Its low glass transition temperature is approximately 25°C and low moisture absorbency is approximately 1% or less by weight. Other materials may exhibit such characteristics and therefore may likewise be suitable as a binder matrix for PSH TIMs. Such materials may provide better adhesion and lower contact resistance than silicones (Jayaraman et al. 2007). Other polymers usable in the curable matrix include siloxanes, olefins, and epoxies. Polymeric resins usable in the PSH include any thermosetting resin (either monomeric or polymeric) that is cross linkable by the curing agent, a metal catalyst, or a hydroxyl group-bearing agent. Resins which meet this requirement include epoxies, phenolics, novalacs (both phenolic and creosotic), polyurethanes, polyimides, bismaleimides, maleimides, cyanate esters, polyvinyl alcohols, polyesters, polyureas, acrylics, polyamides, polyacrylates, polysiloxanes, cyanoacrylates, and the like. Other resin systems are modifiable to be cross linkable by the curing agent, a metal catalyst, or a hydroxyl group-bearing agent. Examples of such resins include acrylics, rubbers (butyl, nitrile, etc), polyamides, polyacrylates, polyethers, polysulfones, polyethylenes, polypropylenes, polysiloxanes, polyvinyl acetates/polyvinyl esters, polyolefins, cyanoacrylates, polystyrenes, and the like (Matayabas and Dani 2003).

Typical conventional PSH TIMs have the following characteristics:

(1) Storage–Store frozen at –40°C. Shelf life at –40°C is 1 year.
(2) Thaw–Allow to warm to room temperature prior to use.
(3) Pot life–8 h at room temperature (below 30°C).
(4) Dispense–Dispense enough material on the die to give a 50–75 μm thick bond line. 0.4 g of PSH per cm^2 of die area.
(5) Cure cycle–150°C for 30–45 min in a preheated oven at a pressure of 30 psi to hold the parts together during the cure.

Graphite-Based Thermal Interface Material

Flexible graphite sheet materials have become an attractive TIM because of their excellent resilience and flexibility to conform well to the mating surfaces, relatively high thermal conductivity (>3 W/m K) in thickness direction, low thermal expansion, thermal stability, and chemical inertness (Luo et al. 2002).

In general, the flexible graphite is prepared from flakes of natural graphite that are intercalated in an acid solution. After the flakes are intercalated they are washed and dried and then exfoliated by exposure to a high temperature for a short period of time. This causes the flakes to expand or exfoliate in a direction perpendicular to the crystalline planes of the graphite. The exfoliated graphite flakes are vermiform in appearance and are therefore commonly referred to as worms. The worms may be compressed into sheets or foils with a density approaching theoretical density although a density of about 1.1 g/cm^3 is considered typical for most applications. In addition, for TIM application, the graphite is usually optimized by reducing ash content and choosing proper graphite flake source, flake size, treatment chemistry, expansion thermal conditions, and sheet density. The sheets of flexible graphite can be cut into any desired configuration to suit a particular TIM application (Smalc et al. 2003).

Flexible graphite sheets are porous and have a density that various between 0.60 and 1.40 g/cm^3, considerably lower than the theoretical density of graphite of 2.25 g/cm^3 because the pores are open and interconnected, it is possible to impregnate flexible graphite sheets with various materials to improve their performance for TIM application. In particular, polymeric materials, including mineral oils and synthetic oils, can be added to lower the thermal resistance of the TIMs. Flexible graphite TIMs are ideal for TIM2 application. The typical characteristics of the flexible graphite TIMs include light weight; high thermal conductivity 300–400 W/m K; high heat resistance (in nonoxidizing environment above 3,000°C); and excent EMI shielding efficiency. Materials with adhesive coatings are designed for use in applications requiring low contact resistance, high thermal conductivity at low clamping loads, and ease of application. One example is the TIMs that are manufactured from natural graphite and a polymer adhesive. A pressure sensitive adhesive (PSA) can be applied to one surface of the TIM to adhere the TIM pad to heat sinks, spreaders, etc. This kind of TIM is an excellent replacement for thermal grease PCMs with advantages, such as not separate, dry out or pump out, and excellent contact can be maintained for the life of the assembly (Luo et al. 2002).

Advanced Thermal Interface Materials

In order to manage the escalated need for heat dissipation, advanced TIMs, which promote heat transfer within a package or from a package to a heat sinking device, have a strong need for improvement of thermal dissipation as a result the thermal resistance of interfaces, as a fraction of total junction to ambient resistance, has grown dramatically. Conventional TIMs call for filling a polymeric carrier (grease, PCM, silicone, etc.) with highly conductive particles to produce a material with low to moderate thermal conductivity. These materials work well when gaps between components can be minimized (e.g., bond line thickness of 0.001 in. or less). When gaps are larger, conduction of heat within the interface material (i.e., from particle to particle) dominates the interface thermal resistance and poor performance results. A new class of fiber reinforced interface materials have been developed which overcome this limitation. These materials feature an aligned array of conductive fibers. This structure allows one fiber to span the gap between the two surfaces, resulting in very high thermal performance, even for large gaps. Because the fibers have a high aspect ratio, the material has a high degree of mechanical compliance, making it ideal for application such as interfaces within multichip modules, mobile products, or gap filling applications where variations in interface thickness can be absorbed with little or no thermal penalty. The material has been shown to be very robust with respect to thermal and mechanical cycling, and will not pump out or dry out from the interface during actual use. Meanwhile, nanotechnology-based TIMs also caused great attention and would play a great role in next generation high performance electronic packaging.

Gelvet and Fiber-Reinforced Thermal Interface Materials

Conventional polymer-based TIMs wet out surfaces quite well and provide low thermal contact resistance. To achieve a significant degree of thermal conductivity, however, the material must be highly loaded with thermally conductive particulate or flake. Loading in excess of 60–70 vol% conductive fillers such as alumina, silica, BN, graphite, silver, or other metals is common. Forcing particle to particle contact creates a heat transfer path and increases the thermal conductivity of the polymeric system to approximately 1 W/m K for typical systems and up to 4–8 W/m K for very specialized materials. These conventional interface materials are limited by relatively low thermal conductivity, as the resistance to heat transport generated by particle to particle contact limits the efficiency of the conductive filler used. An alternate to filling a carrier with flake or particulate material has been developed to use an aligned structure of thermally conductive fibers, commercially called Gelvet™. As shown in Figure 8.23, these fibers create a continuous thermal path from one surface to another, and hence give rise to a composite interface material with an inherently high conductivity. As this high conductivity can be achieved with a comparatively low volume fraction of conductive fibers, the TIM can be made very compliant, especially if fibers of suitable aspect ratio (fiber length/fiber diameter) are chosen. The fibers are held in place by some thin layer of adhesive and encapsulated in a gel or elastomeric material to prevent broken fibers from escaping the interface. The encapsulant material is chosen to wet the fibers and result in a tent-like structure at the free fiber tips which gives some degree of wetting out at the fiber tips, while not inhibiting the inherent compliance of the velvet-like fiber structure. Because the thermal conductivity of this structure does not depend on particle to particle contact, some degree of drying out of the encapsulant does not affect thermal performance. Also, this material is easily reworkable and will remain in place and not be subject to pumping out of material

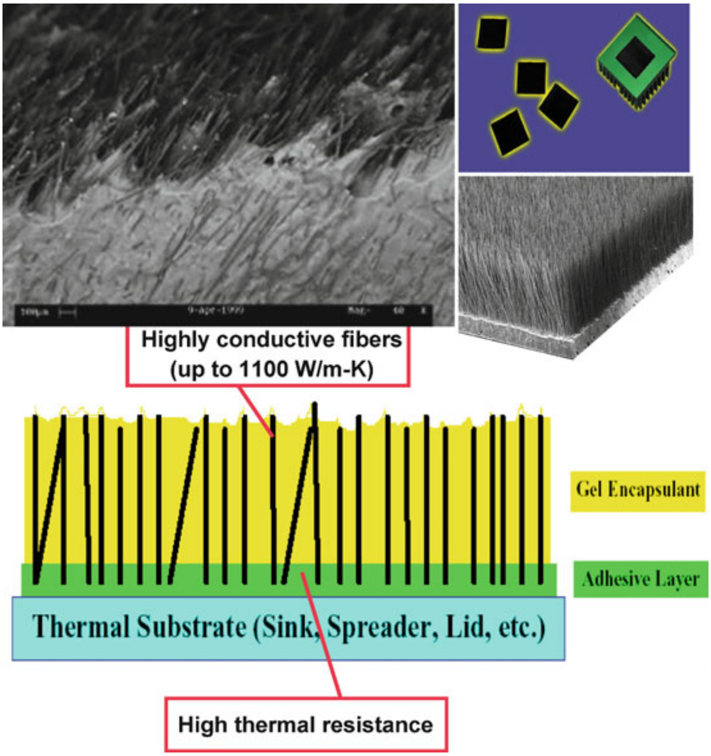


Fig. 8.23 Structure of Gelvet thermal interface material

because all the conductive elements (fibers) are anchored in place. The materials set of choice for this type of interface material will be a high thermal conductivity fiber which has a small diameter, is readily available, and relatively inexpensive. In general, carbon or graphite fibers meet all of these characteristics. For example, 10 μm diameter carbon (graphite) fibers, with axial thermal conductivities of 800 and 1,100 W/m K have been used for the aligned fibers (Dean and Pinter 1999).

The key feature of an aligned fibrous interface material is its inherent high thermal conductivity. When the fibers are aligned in the direction of heat transport (i.e., spanning the interface gap), the theoretical thermal conductivity of the resulting material can be given by (Dean and Pinter 1999)

$$K_{\mathrm{TIM}} = k_{\mathrm{fiber}} A_{\mathrm{fiber}} + k_{\mathrm{polymer}} (1 - A_{\mathrm{fiber}}), \tag{8.14}$$

where k represents thermal conductivity and A the area fraction occupied by the aligned fibers. For a typical structure with 10% of the area occupied by carbon fibers having a conductivity of 1,100 W/m K, this gives a TIM thermal conductivity of approximately 110 W/m K. Actual measurements give a thermal conductivity of 50–90 W/m K for this material (Dean and Pinter 1999).

As the pressure increases, the thermal resistance can decrease dramatically. Benchmarking has indicated that the thinner versions of this material are able to perform on par with typical greases and PCMs for moderate bond line thicknesses and interface pressures. As the mating surfaces deviate from planarity, the effect an increased interface thickness does not significantly affect the thermal resistance of these aligned materials, while the thermal resistance of most other interface materials increases dramatically. This effect is due to the differences in bulk thermal conductivity between the aligned interface materials and conventional materials (Dean and Gettings 1998).

The aligned fibrous structure presents a very compliant interface compared with highly loaded structures. When the fiber aspect ratio is high, it takes very little force to bow, or elastically buckle, the fiber. Compliance of a material may be tailored by varying the type of fiber used or the length of fiber (material thickness), with little thermal penalty, due to the high inherent thermal conductivity resulting from this structure. This compliance is useful in absorbing stack-up tolerances for assemblies or accommodating die of differing height in multichip modules.

This TIM is produced in sheet form and may be preapplied to any component surface or shape. As it resembles a sheet or gasket and maintains this form, the component to which it is attached may be disassembled and reworked without necessitating replacement of the interface material. Numerous assembly cycles for a heat sink application and thousands of cycles for a burn-in application have been observed with little degradation to the interface material. This material has been demonstrated not to pump out in thermal, mechanical, or power cycling, as the fibers are anchored in an adhesive. The carbon fibers do not degrade with temperature increases, hence the properties of the material are not affected by a bake test for an assembly. Through appropriate choice of encapsulant and adhesive, low outgassing, residue, and high temperature applications may also be serviced.

In summary, the features of the Gelvet TIMs include:

- Highly oriented fibers
- Free tips contact mating surface
- Highly conductive graphite fibers (up to 1,100 W/m K) utilized to create a thermal pad with conductivity 6–20 times higher than conventional interface pads (composite $k = 30–100$ W/m K)
- Material may be attached directly to any substrate
- Aligned fiber structure results in a mechanically compliant material
- Thickness of pads may be tailored from 0.020 to 0.100 in.

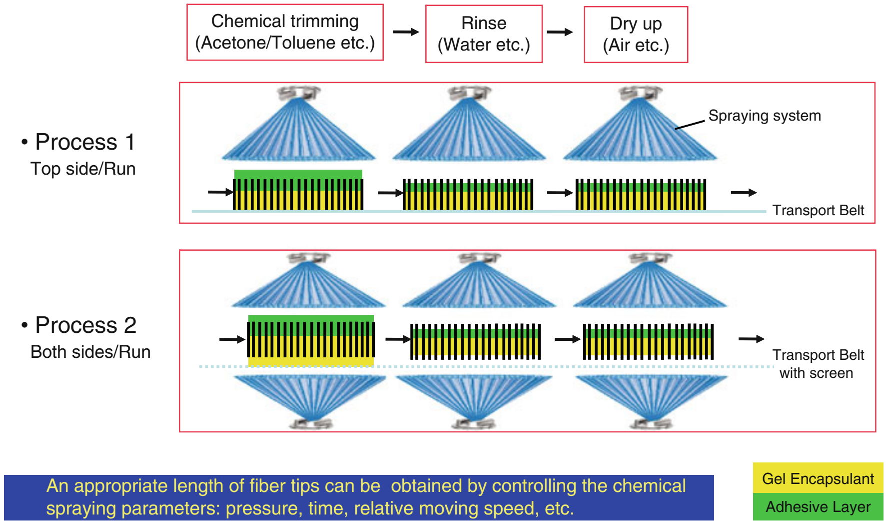
There are some limitations to this type of material. The thickness cannot be reduced much below 0.015 in, as it becomes difficult to properly orient fibers that are shorter than this. As the carbon fibers used are very strong in tension and compression, but brittle in shear, this material does not exhibit good abrasion resistance and is not suitable for applications that require shear resistance. The temperature limits of the preferred adhesives and encapsulating material restrict their use to temperatures under 110°C, although substitutions for these materials may be made to extend the temperature range if a thermal penalty can be absorbed. Also, the selection of carbon fibers produces a material that is electrically conductive, which may be unattractive for some applications.

To modify and improve the performance of the gelvet TIM, the reduction of the thermal resistance at fiber-gel junction can be attempted with a chemical trimming process as shown in Figure 8.24 and aim to meet:

- A preferably orientalized fiber structure can be utilized to create a thermal interface pad able to used for TIM1 or TIM2
- Fiber tips can be exposed out of the surface of the adhesive layer and the gel encapsulant
- The length of the fiber tips can be effectively controlled and matched with the roughness of the mating surface to ensure a good contact
- Exhibits the higher thermal conductivity than that of current Gelvet
- Exhibits relatively low thermal resistance
- Modified TIMs could be generated when using high performance raw materials or modified processes

This requires the proper selection of fiber, adhesive and encapsulant materials:

- Fibers–high thermal conductivity with maximum density
  - Graphite
  - Diamond
  - CNT (if available) or other nano-fibers
  - Metal wires
  - Others



An appropriate length of fiber tips can be obtained by controlling the chemical spraying parameters: pressure, time, relative moving speed, etc.

Fig. 8.24 Schematic surface trimming process to get an appropriate length of fiber tips for minimizing contact thermal resistance at fiber–gel junction

- Adhesive layer–sticky and highly conductive
  - Gel with high thermal conductivity fillers
  - Liquid crystal polymer or its composites
  - Graphite paints or other adhesives with high thermal conductivity
- Encapsulant–balance between compliance and stiffness
  - Gel with stiff filler
  - Liquid crystal polymer or its composites
  - Graphite paints or other adhesives with high thermal conductivity

In fact, Gelvet TIM has been used for thermal interface material between heat sink to die interface, heat sink to package interface, and heat sink to multichip module interface.

In addition to Gelvet™, AF Inter Connector material manufactured by Shin Etsu, for instance, also uses carbon fibers in a silicone matrix with the carbon fibers disposed normal to the interface surface. The AF material acts as an electrical conductor between two devices, while the Gelvet material is designed to conduct heat between heat sinks and heat generating devices. Both of these solutions are designed for electrical nonspace applications and do not use a low- or non-outgassing polymer matrix material. It has also been found that the Gelvet material may also exhibit fiber damage during cutting of the graphitized carbon fiber and may have a less consistent distribution of fiber length (Suzuki et al. 2009).

Accordingly, an improved TIM that uses carbon-based fiber in a low- or non-outgassing polymer matrix have been used for use in contamination-sensitive cases, such as spacecraft applications. The TIM comprises highly thermally conductive (carbon-based) fibers contained, embedded, or immersed, in a low- or substantially non-outgassing polymer matrix material or gel encapsulant. The low- or non-outgassing polymer matrix material comprises high thermal conductivity, small diameter fibers, such as carbon fibers for example, that are disposed substantially normal to interface surfaces, and protrude above at least one of the surfaces of the low- or non-outgassing polymer matrix material. The thermally conductive fibers adjust to and contact surfaces to which they are attached and conform to macroscopic non-planarity of the surfaces. The thermally conductive fibers act as continuous conductors of heat from surfaces to which they are attached. For some applications, the thermally conductive fibers may be cut in a manner that reduces damage. This is achieved by cutting green state ungraphitized fibers to length, instead of cutting graphitized thermally conductive fibers. Heat treatment of the carbon based fibers may be done after the green state thermally conductive fibers are cut to length. The thermally conductive fibers, such as carbon fibers, for example, in the green state (ungraphitized) are cut to a desired length and are then graphitized. The graphitized thermally conductive fibers are then embedded in one or more layers of low- or non-outgassing polymer matrix material having a desired thickness. The graphitized thermally conductive fibers protrude from an interface surface of the low- or non-outgassing polymer matrix material by a predetermined amount. The graphitized thermally conductive fibers and the polymer matrix material securing them are then cured for a prescribed time period and temperature depending on the selected polymer matrix material and the desired end use properties. The polymer matrix material used in the TIM is chosen to pass stringent spacecraft environmental requirements. For example, the polymer matrix material is substantially non-outgassing which means that it contains volatile condensable material of less than 0.1% and has a total mass loss of less than 1.0% per an ASTM E595 procedure. Methods for introducing the graphitized thermally conductive fibers into the polymer matrix material include flocking, mixing, infiltration, electrostatic, preimpregnation, wicking, or vacuum transfer, for example. By using green state thermally conductive fibers, cost is reduced because the green state fibers are significantly less expensive to purchase and are easier to cut to length with less damage. The graphitized thermally conductive fibers may be heat treated to enhance the properties that provide high thermal conductivity. The TIM improves heat transfer between components and/or devices that generate heat and an external environment, such as is provided by a radiator panel, or other heat radiating device, for example, employed on a spacecraft. Also, the polymer matrix material used in the TIM exhibits low outgassing, thus enabling the TIM to be used in a space environment (Bonneville et al. 2001).

Nanotechnology Based Thermal Interface Materials

A new class of nanotechnology based TIMs have been developed, such as CNT-based TIMs, Graphene TIMs, and nano-TIM with adhesion functions that has low thermal resistance, high thermal conductivity and high mechanical strength using electrospinning process. With the electrospinning process, polymer nanofibers with nanoscale diameter can be formed. Nanoparticles such as nano-silver particles, nano- CNT and nanosilicon carbide particles can be embedded into the nanofibers to enhance the thermal conductivity and to reduce the thermal resistivity. This new class of the nanofiber-based composite TIMs can offer high thermal conductivity, low thermal resistivity, similar operation temperature range, and similar degradation behavior, two to five times higher ultimate tensile strength, in comparison with commercially available TIMs. Incorporating adhesion functions into the developed nano-TIMs has been carried out using lamination or direct mixing methods. To achieve this, hot melt adhesive is planed to be directly laminated into the nano-TIM materials to achieve adhesion function. Another method is to directly dissolve thermosets into solutions to achieve the nano-TIMs with adhesion function in the same operation.

Carbon Nanotube Adhesive

CNTs are increasingly finding applications in thermal management materials and are also being considered as potential interface and attachment techniques. Figure 8.25 shows typical CNT thermal interface options. (1) CNT array growths on

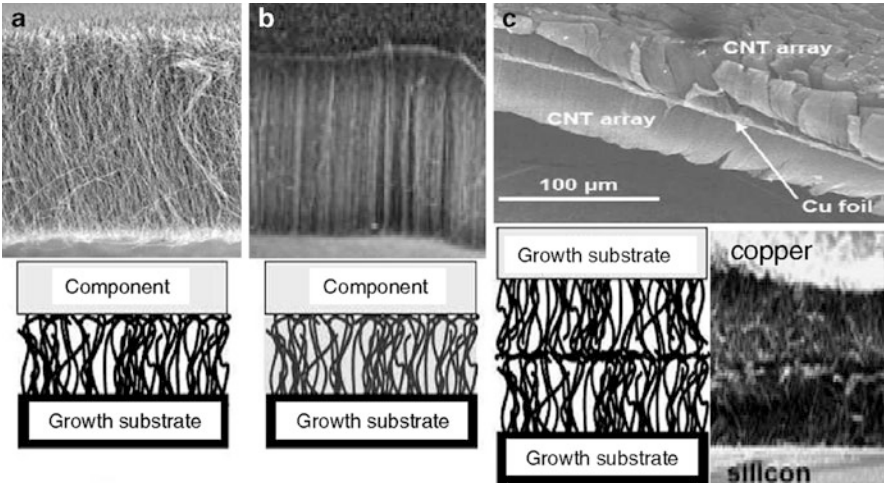


Fig. 8.25 Carbon nanotube (CNT) thermal interface options. (**a**) CNT array growths on one substrate; (**b**) CNT array growths one substrate with filler; (**c**) CNT arrays grow on both substrates and butt against each other with or without copper foil between

one substrate; (2) CNT array growths one substrate with filler; (3) CNT arrays grow on both substrates and butt against each other with or without copper foil between. When grown on a surface in an array, CNTs can provide an extremely large surface-to-volume ratio and bind to each other and to surfaces through van der Waals (vdW) interactions. When acting collectively, vdW forces can provide significant adhesive strength (~12 N/cm^2) regardless of the hydrophobicity of the surfaces. In conjunction with their electrical and thermal conductivity, this adhesive characteristic makes CNTs potentially attractive as a device or substrate attachment material. Typical nanotube dimensions: MWNT diameter 20–30 nm; multiwalled carbon nanotube (MWNT) height 5–500 μm; Spatial density 1,010–1,011 tubes/cm^2; Contact area 4–20 mm^2. With a preload of < 2 kg in the normal direction, the maximum measured adhesive strength for 5–10 μm height arrays to a glass surface was 11.7 N/cm^2 in the normal direction (apparent contact area of 4 mm^2) and 7.8 N/cm^2 in shear (apparent contact area of 8 mm^2). The adhesive energy between MWNT and a glass surface was found to be 20–80 mJ/m^2. The adhesive strength over repeated adhesion and separation cycles degraded, due to the relatively poor adhesion of the MWNTs to their silicon growth substrate. This was improved significantly by adding molybdenum to the catalyst underlayer (Zhang et al. 2008).

Thermal interface measurements for the silicon/MWNT-glass system identified that the dominant interface is between the MWNT layer and the glass substrate (10^{-5}–10^{-6} K m^2/W) which is at least one order of magnitude lower than that of the chemical vapor deposition (CVD) grown MWNT-silicon interface. Basically, adhesion performance is dependent on the tube length, for example, 5–10 μm tubes gave best adhesion. A relatively large preload (2 kg) is necessary to affect a joint. Adhesive strengths were related to apparent contact areas (4–20 mm^2), e.g., smaller contact areas had higher strengths, possibly due to coplanarity or surface embed vertically aligned MWNT in soft polymer films for improved conformity to surfaces. Adhesive energy and strength can be increased through the use of conformable substrates, single-walled CNTs, solder coated fibers, such as indium, or adhesive on the target surface. The vertically aligned nanotubes (15–250 nm diameter) were grown using microwave-enhanced CVD on silicon and copper substrates using a titanium adhesion layer (~10 nm), aluminum buffer layer (~10–20 nm) and nickel or iron catalyst layer (~16–10 nm). For MWCNT-coated silicon to copper interface (CNT array height 7–13 μm, CNT diameter 15–25 nm, CNT density 20–30 × 10^7 CNTs/mm^2, substrate area 10 × 10 mm), thermal interface resistance of 20–37 mm^2 K/W at a pressure of 0.445 MPa. A combination of a CNT array and a PCM (load 0.35 MPa) produced a minimum resistance of 5.2 mm^2 K/W. With 3-ω measurements of vertically aligned CNTs on silicon substrate (CNT array height 13 μm, CNT diameter 10–80 nm), effective thermal conductivity reaches 74–83 W/m K in the temperature range 295–323 K, one order of magnitude higher than the test thermal greases or phase-change materials. In general, the major thermal impedance is at the tube tip substrate interface. The main issues with the current technique are ensuring that the silicon is kept below 350°C during CNT processing (this is not an issue with silicon carbide devices) and the need to apply a clamping pressure (1–4 atm) to effect a joint (Young et al. 2006).

By using vertically aligned CNT array as dry interface material to bridge the interfaces, this technology could perform as a thermally conductive tape that provides not only good thermal conducting ability but also strong mechanical bonding between the mating surfaces. It has been shown that a small fraction of CNTs as filling material could induce a 125% enhancement in thermal transport. This interface material can be directly applied to any interface that needs high thermal conductance. A preload of a few kilograms would be sufficient to create a good contact and adhesion. The bonding of the two mating surfaces is based on the van der Waals interaction between the CNTs and the surfaces which is inversely proportional to the feature size of the structure. Because of the high density and small diameter of the CNTs, the contact of the CNT array with the mating surface could generate a fairly good adhesion force in the order of few Newton per centimeter square (N/cm^2). Benefits of using CNTs as a TIM include: (1) not messy; (2) saves time through ease of installation; (3) eliminates problem of applying the exact amount of grease with each application; (4) CNTs have extraordinary mechanical properties besides the ultra high thermal conductivity. The fine structure of CNTs ensures the filling-in of the cavities at the interface, and ensures direct contact at mating surfaces. (5) Different from other approaches the vertically aligned CNT arrays form parallel paths across the mating surfaces with each path containing one CNT and two junctions at surfaces. This allows a better minimization of the number of junctions and therefore maximization of the thermal conductivity. (6) The high density of CNT array ($>10^{10}$ cm^{-2}) enables a high effective thermal conductance at interface. Different from traditional thermal greases, this interface material could be reusable, detachable, and mechanically robust. Furthermore, it can provide much better thermal performance than the general thermal conductive tapes that are commercially available. A more important advantage of this technology over thermal greases or thermal tapes is that it can work under some extreme environments, such as vacuum, very low and very high temperatures (Zhang et al. 2008).

Potential applications include TIMs of microprocessors and power electronics especially for thermal devices in space, because traditional TIMs could not effectively perform in the space environment.

Graphene-Based Thermal Interface Materials

Graphene-based TIMs have been developed with vertically grown graphene or individual graphene sheets that align perpendicular to the plane of microchips and heat spreaders or heat sinks, providing a superior thermal conduction path from chip to sink. Graphene has extraordinary thermal conductivity ~3,000–5,000 W/m K, and the graphene based TIMs have the advantages of high packing density, rich shapes/geometry, easily functionalized, and possibilities to bond to surface (Chen et al. 2008).

Figure 8.26 shows the concept of TIM with vertically grown graphene sheets between (and bonded to) substrates. Microwave plasma enhanced CVD can be used

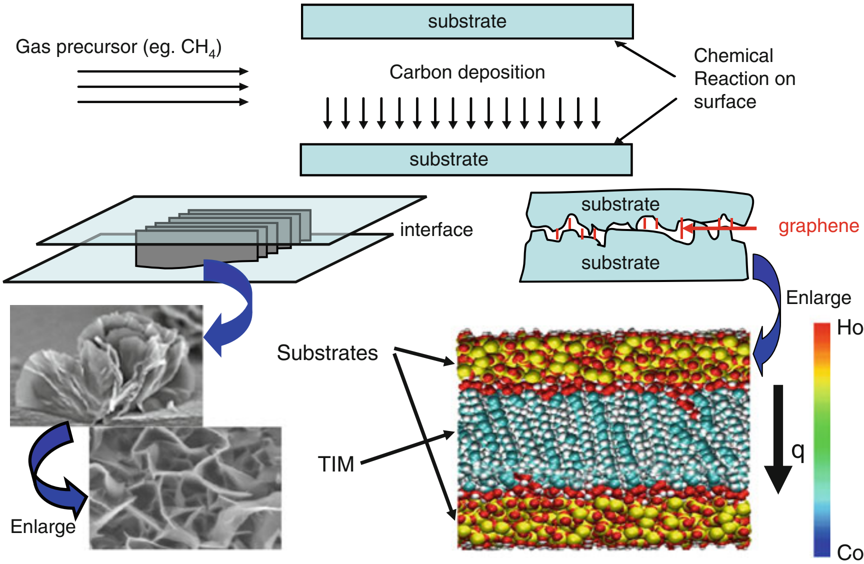


Fig. 8.26 Concept of chemical vapor deposition grown vertical graphene between two substrates as TIM (Chen et al. 2008)

to grow vertically aligned graphene sheets: no catalyst needed, works on almost any substrate, and graphene bonded to substrate surface can have very high filling/packing density. Theoretically predicted thermal conductivity of the vertically grown graphene would be around 1,500 W/m K (Chen et al. 2008).

In addition, graphite oxide is a layered material consisting of hydrophilic oxygenated graphene sheets (graphene oxide sheets) bearing oxygen function groups on their basal planes and edges. Graphite oxide can undergo complete exfoliation in water, yielding colloidal suspensions of almost entirely individual graphene oxide sheets with a mean lateral dimension of approximately 1 μm. Such sheets can be chemically functionalized, dispersed in polymer matrices, and deoxygenated to yield novel composites. Furthermore, graphene paper and graphene oxide paper are synonymous with each other with the only difference being that the oxide in graphene oxide paper is reduced using hydrazene before the individual sheets are stacked together as graphene paper. These graphene oxide sheets can be assembled into a paper-like material under a directional flow, similar to the way buckypaper is formed from CNTs. The graphene oxide paper was made by filtration of colloidal dispersions of graphene oxide sheets through an Anodisc inorganic membrane filter that is fabricated from a unique form of aluminum oxide with a highly controlled, uniform capillary pore structure. The graphene oxide sheets were then air dried and peeled from the filter. The thickness of each graphene oxide paper sample was controlled by adjusting the volume of the colloidal suspension. The thickness of the free-standing graphene oxide paper ranged between about 1 μm and about 30 μm. Well-packed layers through almost the entire cross section of a graphene oxide paper having a thickness of approximately 10 μm. However, graphene paper is different from buckypaper for thermal heat spreading applications. Graphene paper has significant overlap of the individual graphene platelets as compared to buckypaper in which the individual tubes typically form a matrix with the overlap area between individual tubes being significantly smaller than the overlap area between graphene sheets. This overlap results in lower thermal resistance between individual graphene sheets and therefore better heat transport. The thermal resistance at the overlap region of nanotubes is the biggest contributor to the thermal resistance in buckypaper. Graphene paper therefore has a significant advantage to buckypaper. Furthermore, the stacking order of the individual sheets of graphene paper, would give the graphene paper superior thermal conductivity, is not possible in buckypaper because CNTs, being one-dimensional (1-D) structures cannot be stacked like graphene, which are 2-D structures. Third, interlamellar water present between individual sheets of graphene paper, which provides graphene paper with superior thermal conductivity, is not present in buckypaper. The combination of these makes the graphene paper a superior thermal conductor than buckypaper. Given that interlamellar water is present between individual sheets of graphene paper, the individual sheets are held together by hydrogen or covalent bonding. By contrast, the individual sheets in commercially available graphite paper are held together by van der Walls bonding. This distinction between graphene oxide paper and graphite paper indicates that graphene paper may exhibit superior mechanical properties, and in particular superior thermal conductivity properties, as compared with commercially available graphite paper. Specifically, the hydrogen or covalent bonding of the individual sheets in graphene paper would decrease phonon scattering, and therefore increase the thermal conductivity of the graphene paper. The measured thermal diffusivity of graphene paper having a thickness of about 14 μm (0.014 mm) using a laser flash technique apparatus is about 30 cm^2/s (2,929.72 mm^2/s). The specific heat was measured to be about 0.8 J/gK using a differential scanning calorimetric technique. The density was measured to be about 1.83 g/cm^3 using He Pycnometry. Subsequently, the thermal conductivity of the graphene paper was calculated to be about 44 W/cm K. Based on the measurements of the thermal conductivity, it was envisioned that individual sheets of the graphene paper could be aligned to be perpendicular to the plane of a heat source and heat spreader or heat sinks, thus providing a superior conduction path from the heat source to the heat sink (Tilak et al. 2010).

Thermal Interface Materials Selection and Application

The essential purpose of TIMs is to maintain effective transfer of heat from hot chips to dissipating devices such as heat sinks or spreaders. As heat flows, it encounters thermal resistances that impede overall heat transfer. TIMs reduce the most problematic of these, the contact resistance between the mating parts (heat source–heat sink). Air gaps significantly limit heat flow from the hot component into the sink or spreader. An effective TIM replaces the gaps created by the nonsmooth mating surfaces with a material whose thermal conductivity is much greater than that of air. Basically, it replaces poor conduction from point contacts and air to enhanced conduction through solids. The effectiveness of a thermal-interface material can enhanced by high thermal conductivity filler or reinforcement and low thickness of the interface material and low thermal-contact resistance between the interface material and each mating surface.

Commercial TIMs Selection and Application

As the mating surfaces are not perfectly smooth, the interface material must be able to flow or deform in order to conform to the topography of the mating surfaces. If the interface material is a fluid, grease, or paste, it should have a high fluidity or workability so as to conform and have a small thickness after mating. On the other hand, the thermal conductivity of the grease or paste increases with increasing filler content, and this is accompanied by decrease in the workability. Without filler, as in the case of oil, the thermal conductivity is poor. A thermal-interface material in the form of a resilient thermal-conductor sheet (e.g., a felt consisting of conducting fibers clung together without a binder, a resilient polymer-matrix composite containing a thermally conducting filler, or flexible graphite) usually cannot be as thin or conformable as one in the form of a fluid, grease, or paste, so its effectiveness requires a very high thermal conductivity within it. Therefore, it is important to balance all factors when choosing a proper TIM.

Most TIMs are polymer-based composites loaded with heat-conducting filler particles. Common fillers include aluminum oxide (alumina), BN, aluminum nitride, and magnesium oxide. Metal fillers, such as silver, can be used where electrical isolation is not needed. Some level of pressure is usually needed between the mating surfaces to compress filler particles and make the material flow into the surface irregularities to reduce contact resistance. Once in place, a TIM's effective thermal resistance comprises the bulk resistance of the material and the contact resistance between the TIM and its mating surfaces. For instance, thermal-interface materials used in commercial computing systems are typically made up of a polymer matrix in combination with highly thermally conductive fillers (metal or ceramic), such as thermal epoxies, PCM, thermal greases, and gels. At small interface thicknesses, it is seen that the choice of the interface material is a function of both the contact resistance and the bulk conductivity. The particular material chosen depends on the relative magnitude of these two entities at the target design thickness. Performance considerations as well as cost and manufacturability concerns, inevitably result in tradeoffs that are made during interface material selection. Matrix selection is typically driven by its compatibility with filler, its mechanical properties, its ability to wet the mating surfaces, and its viscosity. The maximum filler loading that can be achieved is dictated by the thermodynamic wetability of the filler by the matrix and by the polymer viscosity. The polymer matrix also allows tailoring of the desired mechanical properties of the interface material under use conditions. Epoxy resins are used when high modulus and adhesion are targeted, whereas silicones are used for low-modulus and stress-absorbing applications. Lower surface energy materials are used to act as a matrix since they improve the wetability at the mating surfaces. Common examples of the use of silicones are the polymer materials. The key ingredient in the interface material is the filler, which is responsible for heat conduction. The fillers are dispersed in a polymeric matrix, which typically has poor thermal conductivity, for handling and processability. The important filler properties are bulk thermal properties, morphology (size and shape), and distribution. To reduce the contact resistance, filler surface treatments (coating) are also critical for ensuring optimum filler and matrix thermodynamic wetting. Ceramic powders such as alumina and magnesium oxide are commonly used due to their lower cost and dielectric properties. Further thermal enhancement is achieved through more conductive particles such as aluminum nitride or BN. These fillers provide a five- to tenfold improvement in bulk thermal conductivity, but due to more elaborate manufacturing techniques, cost 10 to 100 times that of their ceramic counterparts. For higher performance, metal particles such as silver and aluminum are used. Silver is chosen mainly for its very high bulk thermal conductivity. Aluminum provides a balance between the bulk thermal conductivity and density (high volume loading can be achieved because of low specific gravity). Issues such as physical design tolerances, positive pressure at the interface, warpage, and tilt and flatness of the mated surfaces have a direct influence on the thickness of the interface as well as the degree of wetting. Of particular interest is the tradeoff between the flatness (macroscopic) of the surface and the cost of machining. Warpage issues can be alleviated by the choice of assembly materials to lower the processing temperature as well as the CTE mismatch between materials. Interface pressure becomes a key factor with collapsible materials; this is controlled through design. The interaction of filler particles with microstructural asperities at the mated surfaces determines the degree of compaction and wetting at the interface. Materials in a semisolid or liquid state need to be dispensable. A typical tradeoff is that a higher degree of filler loading (to reduce thermal resistance) translates into increased viscosity of the material, which in turn affects the manufacturing throughput (Viswanath et al. 2000).

While thermal interfaces and TIMs are often considered well into the design process, several factors can be summarized as below when choosing a TIM (NeoEase 2010):

(1) *Thermal impedance* is the single most important specification measured in degrees K m^2/W. Thermal impedance is an application-specific measure of the ratio of the temperature difference between two mating surfaces to the steady state heat flow through them. Thermal impedance usually decreases with added mounting pressure and contact area, but increases with the thickness of the TIM.

(2) *Thermal conductivity*, in W/m K, measures a material's ability to conduct heat regardless of its thickness. A bulk measurement, thermal conductivity values can be used for comparing TIMs, but it does not describe a TIM's ability to minimize contact resistance in an application.

(3) *The gap space* between the heat source and the heat spreader. As a rule, the thinner the TIM the better, but because mating surfaces are never perfectly flat, a minimum material thickness may be needed to accommodate nonflatness issues.

(4) *Surface flatness* of mating surfaces is important for determining the type of material. If both surfaces are flat, grease or thin films would be ideal choices, but that is seldom the case. Plastic ICs are typically concave in the center and if the heat sink is extremely flat, the contact area would be limited to the periphery leaving an air pocket in the center.

(5) *Electrical isolation*, measured in kV, is sometimes needed. Silicone-based TIMs provide this property, along with thicker materials such as gap fillers. Thinner PCMs and, greases may not be reliable electrical insulators. Solder and graphite are electrically conductive.

(6) *Compressibility* is important when working with irregular surface and when covering a number of components. If heat and excess pressure are applied to a silicone-based TIM, silicone can escape and migrate along the printed circuit board. Without sufficient pressure there may be excess thermal resistance across the interface.

(7) *Temperature range* in the interface determines which materials can be used. Silicone TIMS, e.g., gap fillers are rated to higher temperatures than silicone free interface materials.

(8) *UL flame class rating*. A UL flammability rating requirement is needed for many TIM applications. Most of these materials are available with V-0 ratings, which will meet most needs.

(9) *Silicone or silicone free*. Silicone is an excellent thermal material with a high temperature range but some applications, e.g., in space, cannot use it due to outgassing.

(10) *Ease of application*. The method of attachment is a cost and performance decision. Most small heat sinks are attached with a double sided thermal adhesive tape. Larger heat sinks require mounting hardware. Adhesives can be added to both or one side of the thermal material. However, with a layer of adhesive, thermal impedance will be increased.

(11) *Utility*. How easy are the materials to work with in a manufacturing environment? How easy are they to rework when heat sinks must be removed? Some gap fillers can be reused, but PCMs and grease must be replaced.

(12) *The long-term stability* of the material depends on such factors as the usage temperature, time, application, and material properties.

The characteristics of typical TIMs would be described and compared as below (NeoEase 2010).

PCMs undergo a transition from a solid to a semisolid phase with the application of heat from the operating processor and a light clamping pressure. The semisolid PCM readily conforms to both surfaces. This ability to completely fill the interfacial air gaps and surface voids, usually under light clamping pressure, allows performance comparable to thermal grease. While less “runny” than grease, PCMs contain wax and once the melt-on temperature is reached, they may flow out of tight areas. Recently introduced phase-change type materials are not wax-based and will not drip. At room temperature these materials are firm and easy to handle. This allows more control when applying the solid pads to a heat sink surface. After installation, some phase-change pads create a strong adhesive bond between the processor and the heat sink. Exercise caution when removing the heat sink from the processor. A slight twisting or rotating movement should help to remove the heat sink. Using strong force to remove the heat sink can damage the processor.

Thermal greases typically are silicones loaded with thermally conductive fillers. They do not need curing and they can flow and conform to interfaces. They also offer reworkable thermal interface layers. It is important to ensure that the proper amount of paste or grease is dispensed prior to installing the heat sink. Too little grease may leave gaps between the heat sink and processor; too much might also cause air gaps and leak material outside the interface. On extended operation and over time, some greases can degrade, pump out, or dry out, which affects thermal transfer performance. Despite these drawbacks, greases are the interface materials of choice in high performance processor applications. Thermal conductivity of high performance thermal greases is in the order of 10 W/m K, which is superior to other TIMs.

One of the largest segments of the thermal interface market, gap fillers are supplied in different thicknesses and can cover large segments of a board. Effective materials can fill gaps up to one-quarter inch with a soft, highly thermally conductive interface. Gap fillers can blanket over multiple components of varying height to conduct heat into a common heat spreader. These pads are often used when low compression forces are required, therefore, high compressibility is an important feature. Gap fillers can be custom molded, and new form-in-place gap filler compounds are an option for high volume automation.

Thermal films provide electrical isolation along with thermal transfer. Their film carriers give superior resistance to tear and cut-through from burrs on heat sinks. This category includes silicone, silicone-free (e.g., ceramic-filled polyurethane), and graphite materials with a wide range of thermal performance and price points.

Thermal pads usually are fabricated by molding nonreinforced silicone with conductive fillers. Reinforcements for thermal pads can include woven glass, metal foils, and polymer films. Thermal pads are typically precut in sizes to accommodate different size components. From a performance standpoint, they are inferior to PCMs and thermal grease, but offer a practical, low cost TIM solution in many applications with less cooling requirements.

Graphite films are electrically conductive, have a low cost, and have been used for a long period of time. Graphite films are effective in very high temperatures (up to 500°C). The oriented fibers can be laminated in a horizontal plane resulting in very different thermal conductivity measurements. For example, the thermal conductivity can be 7.0 W/m K on the x-axis and 150.0 W/m K on the y-z axis.

Most small heat sinks are attached to components with a double-sided PSA thermally conductive tape. Factors for tapes include peel strength, lap- and die-shear strength, holding power, and thermal resistance. Thermally conductive adhesive tapes are considered to be convenient for heat sink attachment with mid-range thermal performance. While they replace mounting hardware, thermal tapes often have problems with the lack of flatness on component surfaces. Plastic ICs usually are concave in the center and heat sink surfaces vary as well. This can result in air gaps in the interface. One thermal adhesive tape consists of a finely woven nickel coated copper mesh that conforms closely to irregular mounting surfaces varying up to 50% of its thickness.

Thermal adhesives are one- or two-component systems containing conductive fillers. They are typically applied via dispensing or stencil printing. These adhesives are cured to allow for cross linking of the polymer which provides the adhesive property. The major advantage of thermal adhesives is that they provide structural support, therefore eliminating the need for mechanical clamping.

Thermal gels are low modulus, paste-like materials that are lightly cross linked. They perform like grease with respect to their ability to conform to surfaces, while displaying reduced material pump out.

Metallic TIMs can be made in many different forms and are no longer limited to solder applications. In some applications metallic TIMs are totally reworkable and recyclable. The need for better performing TIMs in such devices as power amplifiers and insulated-gate bipolar transistor (IGBT) modules have prompted exploration of other types of metallic TIMs such as liquid metals, phase change metals, and soft metal alloys. The soft or compressible metal TIM is the most easily adopted metallic TIM because it does not need to be reflowed or contained in a gasket like a solder or liquid metal. Metallic TIMs are very thermally conductive, reliable, and in the case of compressible metals, easily adopted. A new hybrid material consists of a thermally conductive silicone film on one side bonded to a copper film. The advantage of this material is that it can be used to manufacture flex circuits as well as provide electromagnetic interference and RFI (Radio Frequency Interference) noise protection.

Thermal interfaces are often considered late in the design stages of cooling systems. This is not the best practice as TIMs can be the limiting factors in the expense of thermal management designs. With more and more excess heat to be dealt with, there is a steady demand for higher performing TIMs. Used effectively, TIMs can help reduce the size of heat sinks and the need for larger fans. The extended benefit is that an effective TIM is a faster, easier applied, and less costly solution than changing heat sinks or redesigning a chassis.

Future Directions

The focus of future research and application should be on understanding the reliability and performance degradation of TIMs. Current commercial TIMs are capable of providing a thermal resistance between 0.03 and 0.1°C cm^2/W; however, due to degradation at large exposures to high temperatures, the thermal performance can degrade severely depending on the temperature of the processor and time of exposure. There is no mechanistic understanding of these degradations. Fundamental physics-based modeling is needed to relate the degradation of the polymer properties to thermal properties of the polymer composites. Use of nanoparticles and nanotubes is almost inevitable; however, any research in this area should take the performance of the current commercially available TIMs as benchmark. Research should also focus on minimizing the total thermal resistance rather than just increasing the thermal conductivity. A physics-based model for the contact resistance between the particle-laden TIMs and the substrate is still incomprehensive. Contact resistance will become important for thin highly conducting TIMs. Modeling of the CNT concepts will be also needed in the future due its promise as interface material (Prasher 2006).

Summary

TIMs play a key role in thermally connecting various components of the thermal management solutions. As electronic assemblies become more compact and increase in processing bandwidth, escalating thermal energy has become more difficult to manage. The major limitation has been nonmetallic joining using poor TIMs. The interfacial, versus bulk, thermal conductivity of an adhesive is the major loss mechanism and normally accounts for an order magnitude loss in conductivity per equivalent thickness. The next generation TIM requires a sophisticated understanding of material and surface sciences, heat transport at submicron scales, and the manufacturing processes used in packaging of microelectronics and other target applications. Only when this relationship between bond line manufacturing processes, structure, and contact resistance is well understood on a fundamental level will it be possible to enhance interfacial thermal conductance and advance the development of miniaturized microsystems. TIMs are widely needed to improve thermal contacts for facilitating heat transfer in electronic packaging, such as that associated with the flow of heat from a microprocessor to a heat spreader or a heat sink in a computer. A TIM is commonly in the form of paste, solder, or a resilient sheet that serves to fill a gap between the two adjoining surfaces. The performance of a TIM is enhanced by conformability of the interface material to the topography of the mating surfaces because the air residing in the valleys in the surface topography is thermally insulating and should be displaced by the interface material.

Any engineering surface of the electronic components is rough on a microscopic level, due to the presence of microscopic asperities. When two such rough surfaces come in contact during assembly of electronic packaging, the actual contact occurs only at a few discrete spots, usually at the high points of the two mating surfaces. Typically, the ratio of real contact area to apparent contact area is approximately 1–2%. Heat flowing from one body into the other is constricted to flow through the actual contact spots because the thermal conductivity of the solid contact spots is much higher than that of the surrounding gap which is filled with air in most electronic applications. TIMs are often inserted between the surfaces of a contact pair to reduce the thermal contact resistance. Although they typically have lower thermal conductivity than the substrate, they are highly compliant and hence under the application of relatively small contact pressure, deform to conform to the geometry of the adjacent rough surfaces. A part of the low thermal conductivity gas present is thus replaced by a higher conductivity material. This leads to a decrease in the constriction of the heat flow lines, and therefore, an increase in the contact conductance. The heat transfer of these complex joints is governed by contact pressure; number, size, and shape of contact spots and voids; types of fluid in voids; pressure of fluid in voids; hardness and flatness of contact surfaces; modules of elasticity of contact surfaces; surface cleanliness; and property of the TIM used in the joint.

The thermal conductivity of conventional polymeric TIMs generally does not exceed about 5 W/m K and is typically less than about 1 W/m K. However, metallic TIMs that form thermal interfaces with effective thermal conductivities of about 50 W/m K or greater will be the alternative to meet increasing thermal management requirement of high performance electronics. Most metallic TIMs may also exhibit a favorable solder or wetting behavior upon reflow which facilitates a low thermal interfacial resistance. During reflow, the solder and substrate are heated, the solder melts and wets by surface tension and/or local surface alloying. The interfaces consist of intermetallics or interdiffused metals with thermal properties that are frequently less desirable than those of the bulk TIM metal but much better than polymeric TIMs. In addition, the reflow or active bond process can also help to form reliable thermal interfaces. Metallic TIMs, however, can fail in certain applications due to the relatively large differences between the coefficients of thermal expansion of the TIM and the semiconductor and/or heat sink components and the lack of compliance. To take advantage of the metallic TIMs and avoid their disadvantages, a great many metallic TIMs have been developed and offered different characteristics for selection. Such metallic TIMs typically include reflow solders and active bond process, nonreflow solders and LMAs, composite solders and hybrid metallic solder materials, as well as gold–gold interconnection.

If the metallic TIMs are mainly suitable to TIM1 applications, organic TIMs would mostly be used for TIM2 application, although some metallic or organic TIMs have been developed for both TIM1 and TIM2 applications. With advances in packaging technology, the proper selection of a TIM has become more complicated as each application will have different design requirements. The final selection will encompass material properties and process considerations beyond the thermal performance of the material. Compliance, thickness, processing, and response to reliability conditioning are key considerations when engineering the final package. To conform the diversified requirements of advanced processor and packaging technology, different formats of organic TIM have been developed and commercialized such as various thermally conductive elastomers, thermal greases, PCMs, and PSH materials. Despite the maturity of the organic TIM market, there continues to be a need for higher performance and value-added materials. The performance requirement for a TIM encompasses more than thermal performance but a total solution: low thermal resistance across a bond-line, high thermal conductivity, reworkability, sufficient thickness to accommodate non-planarity, compliance for thermal mismatch, preapplication to heat spreader (TIM1) or a heat sink (TIM2) for speed of assembly, and low cost. For instance, both grease and PCMs possess low thermal resistance due to their liquid nature at operating temperature and thin bond-line, however, each possess drawbacks. The reliability and messy nature of grease is a concern, whereas the reworkability and low thermal conductivity for PCMs are drawbacks. Pad and film formats offer many advantages from a processing and packaging perspective, but traditionally, their performance is not as high as grease or PCM. There exists a strong need for high-performance organic TIMs as the strength of those TIMs makes them useful for both TIM2 and TIM1 applications. The emerging high performance organic TIMs include PSH and advanced thermally conductive elastomers. Meanwhile, flexible graphite sheet materials have become an attractive thermal-interface material because of their excellent resilience and flexibility to conform well the mating surfaces, relatively high thermal conductivity (>3 W/m K) in thickness direction, low thermal expansion, thermal stability, and chemical inertness.

In addition, a new class of fiber reinforced interface materials have been developed, which feature an aligned array of conductive fibers. This structure allows one fiber to span the gap between the two surfaces, resulting in very high thermal performance, even for large gaps. Because the fibers have a high aspect ratio, the material has a high degree of mechanical compliance, making it ideal for applications such as interfaces within multichip modules, mobile products, or gap-filling applications where variations in interface thickness can be absorbed with little or no thermal penalty. The material has been shown to be very robust with respect to thermal and mechanical cycling, and will not pump out or dry out from the interface during actual use. Furthermore, nanotechnology-based TIMs have also caused great attention and would play a great role in next generation high performance electronic packaging.

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