

Sodium Silicate Based Thermal Interface Material for High Thermal Contact Conductance

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Sodium silicate based thermal interface pastes give higher thermal contact conductance across conductor surfaces than polymer based pastes and oils, due to their higher fluidity and the consequent greater conformability. Addition of hexagonal boron nitride particles up to 16.0 vol. percent further increases the conductance of sodium silicate, due to the higher thermal conductivity of BN. However, addition beyond 16.0 vol. percent BN causes the conductance to decrease, due to the decrease in fluidity. At 16.0 vol. percent BN, the conductance is up to 63 percent higher than those given by silicone based pastes and is almost as high as that given by solder. Water is almost as effective as sodium silicate without filler, but the thermal contact conductance decreases with time due to the evaporation of water. Mineral oil and silicone without filler are much less effective than water or sodium silicate without filler. [S1043-7398(00)00402-3]

Introduction

Insufficiently fast dissipation of heat is the most critical problem that limits the reliability and performance of microelectronics. The problem becomes more severe as electronics are miniaturized, so the further miniaturization of electronics is hindered by this problem. The problem also accentuates as the power (voltage and current) increases, so the power is restricted by the heat dissipation problem. Excessive heating resulted from insufficient heat dissipation causes thermal stress in the electronic package. The stress may cause warpage of the semiconductor chip (die). The problem is compounded by thermal fatigue, which results from cyclic heating and thermal expansion mismatches. Thermal fatigue commonly causes failure of soldered joints, due to the work hardening of the solder under cyclic thermal stress. Since there are many soldered joints in an electronic package, soldered joint failure is a big reliability problem.

The use of materials with high thermal conductivity and low thermal expansion for heat sinks, lids, housings, substrates and die attach is an important avenue for alleviating the heat dissipation problem. For this purpose, metal-matrix composites (such as silicone carbide particle aluminum-matrix composites) and polymer-matrix composites (such as silver particle filled epoxy) have been developed. However, another avenue, which has received much less attention, is the improvement of the thermal contact between the various components in an electronic package (e.g., between substrate and heat sink). The high thermal conductivity of the individual components cannot effectively help heat dissipation unless the thermal contacts between the components is good. Without good thermal contacts, the use of expensive thermal conducting materials for the components is a waste.

The improvement of a thermal contact involves the use of a thermal interface material [1,2], such as a thermal fluid, a thermal grease (paste) or a resilient thermal conductor. A thermal fluid or grease is spread on the mating surfaces. A resilient thermal conductor is sandwiched by the mating surfaces and held in place by pressure. Thermal fluids are most commonly mineral oil. Thermal greases (pastes) are most commonly conducting particle (usually metal or metal oxide) filled silicone [3–6]. Resilient thermal conductors are most commonly conducting particle filled elastomers. Out of these three types of thermal interface materials, thermal

greases are by far most commonly used. Resilient thermal conductors are not as well developed as thermal fluids or greases.

As the materials to be interfaced are good thermal conductors (such as copper), the effectiveness of a thermal interface material is enhanced by high thermal conductivity and low thickness of the interface material and low thermal contact resistance between the interface material and each mating surface. As the mating surfaces are not perfectly smooth, the interface material must be able to flow or deform, so as to conform to the topology of the mating surfaces. If the interface material is a fluid, grease or paste, it should have a high fluidity (workability) so as to conform and to 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 a filler, as in the case of an oil, the thermal conductivity is poor. A thermal interface material in the form of a resilient thermal conductor sheet (e.g., a collection of conducting fibers clung together without a binder, and a resilient polymer-matrix composite containing a thermally conducting filler) 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.

Thermal greases and pastes have all been used on polymers, particularly silicone. A material which has not been previously investigated for any type of thermal interface material is sodium silicate (water glass). In this work, we found that the use of sodium silicate in paste of silicone results in a superior thermal paste, as indicated by a much higher thermal contact conductance. Sodium silicate is not a polymer, but is a liquid comprising water and $\text{Na}_2\text{O} \cdot x\text{SiO}_2$. It is most commonly used as an adhesive. After application, it dries, but it can be dissolved in water, thus facilitating repair.

In addition to showing the superiority of sodium silicate based thermal paste over silicone based thermal paste, this paper provides a comparative study of various thermal interface materials, including sodium silicate with and without boron nitride particles at various volume fractions (this work), silicone with and without boron nitride particles (this work), zinc oxide particle filled polymers, polytetrafluoroethylene (PTFE) particle filled perfluoropolyether, graphite particle filled epoxy, mineral oil and solder. In contrast to polymer-based or oil-based particle filled pastes, sodium silicate based pastes do not exhibit the large thermal expansion mismatch that is characteristic of polymer-based or oil-based

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pastes, thereby avoiding the phenomenon in which the filler separates from the oil or polymer upon thermal cycling due to thermal expansion mismatch.

Experimental Methods

Materials. The sodium silicate liquid used with or without boron nitride particles is Siliceous-40 from Occidental Chemical Corp., Dallas, Texas. It consists of water and 33.8 wt. percent $\text{Na}_2\text{O} \cdot x \text{SiO}_2$, where x corresponds to a weight ratio of $\text{SiO}_2:\text{Na}_2\text{O}$ of 3.22. The specific gravity is 1.40. It is a colorless liquid.

The silicone (single component) used with or without boron nitride particles is polydimethylsiloxane (silanol) from United Chemical Technologies, Inc., Bristol, Pennsylvania.

The boron nitride particles used as a filler in sodium silicate liquid or silicone are Polartherm 180 from Advanced Ceramics Corp., Cleveland, Ohio. The particle size is 5–11 μm . The thermal conductivity is 280 W/m.K.

The zinc oxide particle filled silicone used in the comparative study is 340 silicone heat sink compound from Dow Corning Corp., Midland, Michigan. A zinc oxide particle filled polymer (not silicone) used in the comparative study is 1978-DP heat sink compound from Tech Spray, Inc., Amarillo, Texas.

The PTFE particle filled perfluoropolyether used in the comparative study is RT-15 Fomblin perfluorinated grease from Ausimont USA, Belle Mead, New Jersey. The PTFE is solid particles and amounts to 15–30 wt. percent. Perfluoropolyether serves as the base oil, while the PTFE particles serve as the thickener.

The graphite particle filled epoxy used in the comparative study is Grade E-1 non-hardening heat transfer cement from Thermon, San Marcos, Texas.

The mineral oil used in the comparative study is OR fluid from Paratherm Corp., Conshohocken, Pennsylvania. The solder used was Sn-Pb eutectic solder from Kester Solder, Des Plaines, Illinois.

Sample Preparation. Boron nitride particle filled sodium silicate paste was prepared by mixing boron nitride particles, sodium silicate liquid and water in the weight ratio 2.30:1.00:3.80, 1.80:1.00:3.24, 1.63:1.00:3.24, and 1.40:1.00:2.94 for 18.0, 17.3, 16.0, and 15.3 vol.% BN, respectively. Mixing was conducted using a ball mill for 4–5 h.

Boron nitride particle filled silicone paste was prepared by mixing boron nitride particles and silicone in the weight ratio 0.41:1.00. Mixing was conducted using a ball mill for 5 h. The boron nitride volume fraction in the paste was 14 percent.

In preparing both sodium silicate based paste and silicone based paste, a surfactant was added to decrease the surface tension and increase the wettability of the particles with the fluid.

Various thermal interface materials were sandwiched between the flat surfaces of two copper disks, which had diameter 12.8 mm and thickness 1.16 mm for one disk and 1.10 mm for the other disk.

Testing. The thermal contact conductance between two copper disks with and without a thermal interface material was measured using the transient laser flash method. The pressure on the sandwich was controlled at various values from 0.23 to 1.15 MPa. The thickness of the thermal interface material was 0.001 in. (25 μm), unless noted otherwise. The finite element program ABAQUS was used to calculate the thermal contact conductance through temperature versus time curves, which were experimentally obtained.

There are several theoretical assumptions in this transient laser flash test for solving the heat conduction equation.

- 1 We assume no heat transfer between sample and environment except for the absorption of laser energy by the sample.
- 2 We assume the laser energy is uniformly absorbed on the surface of the sample.

3 We assume one-dimensional heat flow.

4 We assume that the thermal contact conductance between the two copper disks is uniform.

5 We assume no thickness and no heat capacity for the interface material between the two copper disks.

The governing equation for transient heat conduction for the two copper disks is

$$\frac{\partial^2 T_i}{\partial x^2} = \frac{1}{\alpha_i} \frac{\partial T_i}{\partial t}, \quad i = 1, 2. \quad (1)$$

The boundary conditions and initial conditions are

$$\begin{aligned} \frac{\partial T_1}{\partial x} &= 0 \Big|_{x=d_1} \\ k_1 \frac{\partial T_1}{\partial x} &= k_2 \frac{\partial T_2}{\partial x} \Big|_{x=0} \\ \frac{\partial T_1}{\partial x} &= \frac{C}{k_2} (T_1 - T_2) \Big|_{x=0} \\ \frac{\partial T_2}{\partial x} + \frac{Q}{k_2} &= 0 \Big|_{x=-d_2} \\ T_i &= 0 \Big|_{t=0}, \quad (i = 1, 2), \end{aligned} \quad (2)$$

where T is the temperature, α is the thermal diffusivity of copper, k is the thermal conductivity of copper, C is the thermal contact conductance, Q is the laser energy per unit area absorbed on the surface of the sample, and d is the thickness of a copper disk. The subscripts 1 and 2 correspond to disk no. 1 and disk no. 2. These boundary conditions and initial conditions were input to finite element program ABAQUS for calculation by the thermal boundary element method.

A Coherent General Everpulse Model 11 Nd glass laser with a pulse duration of 0.4 ms, a wavelength of 1.06 μm and a pulse energy up to 15 J was used for impulse heating. The laser power was adjusted to allow the temperature rise of the sample to be between 0.5°C and 1.0°C. Both surfaces of each copper disk (diameter 12.60 mm) had been mechanically polished. The upper surface of disk no. 1 on which the laser beam will directly hit had been electroplated by black nickel in order to increase the extension of laser energy absorption relative to the extension of reflection (Fig. 1). An E-type thermocouple (no. 1) was attached to the

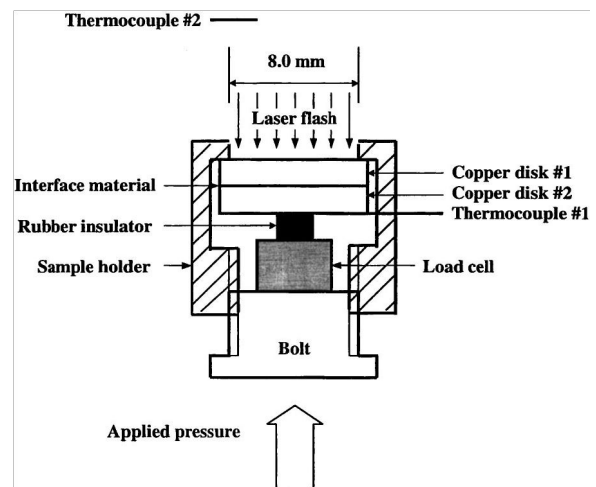


Fig. 1 Experimental set-up for thermal contact conductance testing

back surface of disk no. 2 for monitoring the temperature rise. Another thermocouple (no. 2) of the same type was put ~30 cm above the sample holder to detect the initial time when the laser beam came out. A National Instruments DAQPad-MIO-16XE-50 data acquisition board with a data acquisition rate up to 20,000 data points per second at 16 bites resolution, along with NI-DAQ interface software coded in Visual Basic, was used to monitor the responses of both thermocouples simultaneously. A plexiglass holder (Fig. 1) was used to facilitate pressure application. An Omega LCKD-100 load cell was used for pressure measurement. Calibration using a standard graphite sample was performed before each test in order to ensure measurement accuracy. The data acquisition rate used for each test was adjusted so that there were at least 100 temperature data points during the temperature rise. Five samples of each type were tested for each of five pressures.

Results and Discussion

Table 1 gives the thermal contact conductance for different thermal interface materials and different contact pressures. For each interface material, the thermal contact conductances increase with increasing contact pressure, since the pressure enhances the quality of the interface between the interface material and either copper disk and slightly decreases the thickness of the interface material.

The addition of BN particles to silicone used as an interface material enhances the thermal contact conductance (even though the thickness is increased), due to the high thermal conductivity of BN raising the thermal conductivity of the paste. Sodium silicate (without filler) gives much higher thermal contact conductance than silicone (without filler). Sodium silicate with BN particles is also superior to silicone with BN particles. At a low volume fraction (up to 16 percent) of BN particles, the thermal contact conductance of sodium silicate increases with increasing volume fraction BN. However beyond 16 percent vol. percent BN, the thermal contact conductance decreases with increasing BN volume fraction, due to the decreased fluidity, albeit the increased thermal conductivity within the interface material. Hence, the highest thermal conductance is attained at an intermediate volume fraction of 16 percent BN; the thermal conductance is up to 63 percent higher than those given by silicone based pastes and is less dependent on contact pressure than the silicone based pastes. Water is not as effective as sodium silicate (without BN), even though water has a lower viscosity than sodium silicate (Table 1). Moreover, the thermal contact conductance for water decreases with time due to the evaporation of water. That the thermal contact conductance for sodium silicate (without BN) is only slightly higher than that for water (before significant evaporation) means that the ions in sodium silicate contribute little to the thermal contact conductance. The ions mainly contribute to preventing the evaporation of water.

Table 1 Thermal contact conductance (10^4 W/cm² °C) for various thermal interface materials between copper disks at various contact pressures

Thermal Interface Material	Interface Material Thickness (μm)	Contact pressure (MPa)					Viscosity (cps)
		0.23	0.46	0.69	0.92	1.15	
Solder	25	20.8 ± 0.6 ^c	/	/	/	/	/
Sodium silicate /BN (18.0 vol.%)	25	13.2 ± 0.7	15.5 ± 0.9	16.9 ± 0.3	14.3 ± 0.2	15.8 ± 0.2	/
Sodium silicate /BN (17.3 vol.%)	25	15.1 ± 0.5	15.5 ± 0.4	15.3 ± 0.4	16.4 ± 0.4	16.8 ± 0.5	/
Sodium silicate /BN (16.0 vol.%)	25	18.6 ± 0.7	18.2 ± 0.7	17.8 ± 0.7	17.7 ± 0.5	18.0 ± 0.7	/
Sodium silicate /BN (15.3 vol.%)	25	16.5 ± 0.3	16.3 ± 0.2	15.6 ± 0.2	16.5 ± 0.3	17.6 ± 0.4	/
Sodium silicate	< 25	14.0 ± 0.4	14.1 ± 0.5	15.0 ± 0.4	13.9 ± 0.6	14.0 ± 0.5	206 ^a
Water*	< 25	11.7 ± 0.4	12.8 ± 0.4	/	/	/	1.00 ^a
Silicone/ZnO	25	11.2 ± 0.2	12.2 ± 0.6	13.7 ± 0.7	13.5 ± 1.6	12.3 ± 0.4	/
Silicone/BN	25	11.2 ± 0.7	10.9 ± 1.5	12.0 ± 1.5	13.4 ± 1.4	13.8 ± 0.6	/
Silicone	< 25	2.42 ± 0.04	3.08 ± 0.03	3.34 ± 0.05	4.05 ± 0.05	3.95 ± 0.10	8800 ^b
Polymer/ZnO	25	5.22 ± 0.15	5.16 ± 0.09	5.45 ± 0.12	6.27 ± 0.17	5.91 ± 0.49	/
Perfluoropolyether /PTFE	25	1.76 ± 0.15	2.81 ± 0.22	3.70 ± 0.20	4.65 ± 0.27	5.42 ± 0.45	/
Mineral oil	<25	1.78 ± 0.05	1.70 ± 0.05	2.06 ± 0.22	1.92 ± 0.06	2.02 ± 0.14	85 ^b
Epoxy/graphite	50	0.988 ± 0.004	1.07 ± 0.01	1.31 ± 0.05	1.46 ± 0.08	1.48 ± 0.06	/
None	/	0.598 ± 0.004	0.68 ± 0.01	0.88 ± 0.04	0.99 ± 0.03	1.17 ± 0.05	/

*Values of thermal contact conductance decrease with time due to the evaporation of water.

^aMeasured using the Ostwald Method.

^bValue provided by manufacturer.

^cAt zero contact pressure (not 0.23 MPa). Thickness and heat capacity of solder were not taken into account.

The thermal contact conductances for water (before significant evaporation) and of sodium silicate (without BN) are much higher than that for silicone (without BN), probably because the large molecules in silicone make direct contact between points on the two copper disks more difficult compared to water and sodium silicate, which have small molecules. It is also because of the greater fluidity (lower viscosity, Table 1) of water and sodium silicate compared to silicone making the interface between the interface material and either copper disk better.

Solder gives the highest thermal conductance value in Table 1. This is reasonable due to the high fluidity of molten solder and the metallic nature of solid solder. However, due to the heat involved in soldering, solder cannot be used in many practical situations. The thermal contact conductance of our best sodium silicate based paste (16 vol. percent BN) is almost as high as that of solder.

Out of all the commercial thermal interface materials studied, the ZnO filled silicone of Dow Corning gives the highest thermal contact conductance. However, sodium silicate (even without filler) is superior to this material. PTFE filled perfluoropolyether gives lower thermal contact conductance than the filled polymers at low contact pressures, but is almost as good as the filled polymers at high contact pressures, in spite of its low thermal conductivity. This indicates the importance of the interface between the interface material and either copper disk, as the quality of this interface increases with increasing contact pressure. When the interface material itself is high in thermal conductivity (as for the filled polymers), the quality of this interface is less critical. The mineral oil is less effective than PTFE filled perfluoropolyether, especially at high contact pressures. The effectiveness of mineral oil does not vary much with contact pressure, due to the very high fluidity of the oil compared to PTFE filled perfluoropolyether. On the other hand, mineral oil is less effective than water, partly due to its relatively high viscosity (Table 1). Although mineral oil has a lower viscosity than sodium silicate (without filler), it is inferior as a thermal interface material. This is probably because the large molecules in oil make direct contact between points on the two copper disks more difficult compared to sodium silicate. Graphite particle filled epoxy is inferior to mineral oil, due to the greater thickness resulted from the low fluidity. Without a thermal interface material between the copper disks, the thermal contact conductance is lower than any of the cases with an interface material. Thus, all interface materials are helpful to the thermal contact,

though the effectiveness differs significantly among different interface materials, due to the differences in viscosity and/or thermal conductivity.

Conclusion

Various commercial and non-commercial thermal interface materials (pastes and fluids) were evaluated by using the laser flash method to measure the thermal contact conductance across mating copper surfaces with an interface material between them. Sodium silicate based pastes were found to give higher thermal contact conductance than polymer based pastes and oils, due to their fluidity and the consequent greater conformability. Addition of hexagonal boron nitride particles up to 16.0 vol. percent further increases the conductance of sodium silicate, due to the high thermal conductivity of BN. However addition beyond 16.0 vol. percent BN causes the conductance to decrease, due to the decrease in fluidity. At 16.0 vol. percent BN, the sodium silicate based paste gives a thermal contact conductance that is up to 63 percent higher than those given by silicone based pastes and that is almost as high as that given by solder. Furthermore, the sodium silicate based paste has less dependence on contact pressure than the silicone based pastes. Water is almost as effective as sodium silicate without filler, but the thermal contact conductance decreases with time due to the evaporation of water. Mineral oil and silicone (without filler) are much less effective than water or sodium silicate (without filler).

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