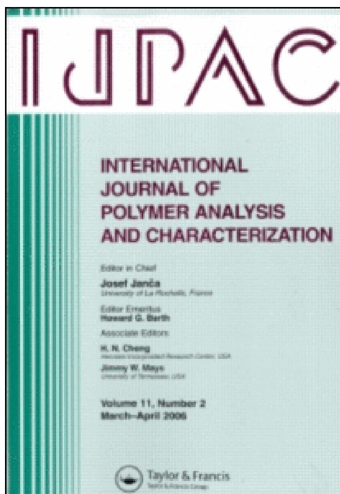
This article was downloaded by:
On: *21 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Analysis of Phase Change Material for Use as Thermal Interface Material

M. H. Nurmawati[a]; K. S. Siow[a]; I. J. Rasiah[b]
[a] Department of Chemistry, National University of Singapore, Singapore [b] Honeywell Electronic Materials, Honeywell (S) Pte. Ltd., Singapore

To cite this Article Nurmawati, M. H. , Siow, K. S. and Rasiah, I. J.(2004) 'Analysis of Phase Change Material for Use as Thermal Interface Material', International Journal of Polymer Analysis and Characterization, 9: 4, 213 — 228
To link to this Article: DOI: 10.1080/10236660490920219
URL: http://dx.doi.org/10.1080/10236660490920219

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

International Journal of Polymer Anal. Charact., 9: 213–228, 2004
Copyright © Taylor & Francis Inc.
ISSN: 1023-666X print
DOI: 10.1080/10236660490920219

Taylor & Francis
Taylor & Francis Group

Analysis of Phase Change Material for Use as Thermal Interface Material

M. H. Nurmawati and K. S. Siow
Department of Chemistry, National University of Singapore, Singapore

I. J. Rasiah
Honeywell Electronic Materials, Honeywell (S) Pte. Ltd., Singapore

Downloaded At: 16:14 21 January 2011

Demands for thermal control in IC chips are more rigorous with increasing power dissipation in electronic devices. The thermal interface material forms an important passage for efficient heat transfer in the chip, and a study has been done to analyze the thermal performance of a particular type of polymeric thermal interface material, phase change material (PCM). A frequent benchmarking characteristic of a thermal interface material is thermal conductivity. As the thickness of the material being used in the real applications gets thinner (typically a few mils), bulk properties like thermal conductivity gives way to interfacial properties as important considerations. To this end, an instrument to suitably measure critical parameters, like the apparent and contact thermal resistance of the thermal interface material, is developed, using the ASTM D5470 as guidelines and modified to suit the semiconductor industry. The measured thermal resistance values obtained in this study allow the evaluation of effective, rather than bulk, thermal properties of the material. In addition, a brief theory of the thermal interface material is described and the properties of the PCM were investigated using the instrument. Other crucial properties that contribute to the efficiency of heat transfer were also analyzed. Characteristics like the bulk thermal conductivity, melting enthalpy, specific heat capacity, and contact

Received 10 October 2003; accepted 24 November 2004.
Address correspondence to M. H. Nurmawati, Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543. E-mail: g0300257@nus.edu.sg

resistance are employed in fundamental equations to comprehend and predict the temperature profile of cooling heated entities.

Keywords: Heat capacity; Phase change material; Thermal analysis; Thermal interface material; Thermal resistance

INTRODUCTION

Heat dissipation in integrated circuits (IC) packages is becoming vital with chips getting smaller and running at ever increasing speeds. Intel® microprocessors advanced from having 1.5 micron lines on the INTEL386™ [1] to 0.13 micron in the current Pentium® 4[2] within a space of seven years. The International Technology Roadmap for the Semiconductor (ITRS) is continually studying the reduction trend in circuitry lines, which is also called the technology node. Figure 1 is an adaptation from the ITRS reports[3–5]. The thinner these lines become, the denser the circuitry will be, leading to extensive increases in heat generation in microprocessor packages.

The increase in heat flow from IC chips is also apparent in the trend of power dissipation for high-performance chips reported by ITRS as shown in Figure 2. Increasing amount of power dissipated has to be offset by efficient cooling because the maximum junction temperature stays relatively unchanged at 85–90°C.

A major challenge in the semiconductor field is, therefore, the ability to manage the heat in the IC chips without compromising the performance of the device. This management of thermal energy is crucial because heat has many detrimental effects on the device. It has been reported[6] that failure rates have near-exponential dependence on device

Downloaded At: 16:14 21 January 2011

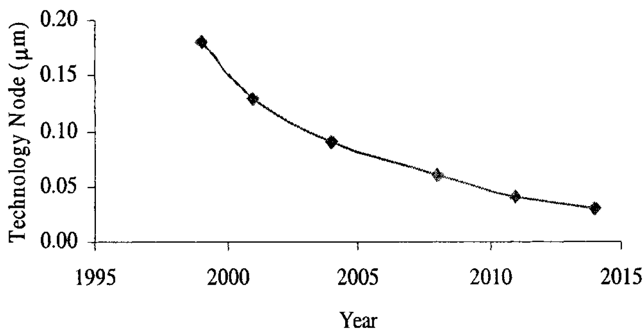


FIGURE 1 Trend in technology node over the years.

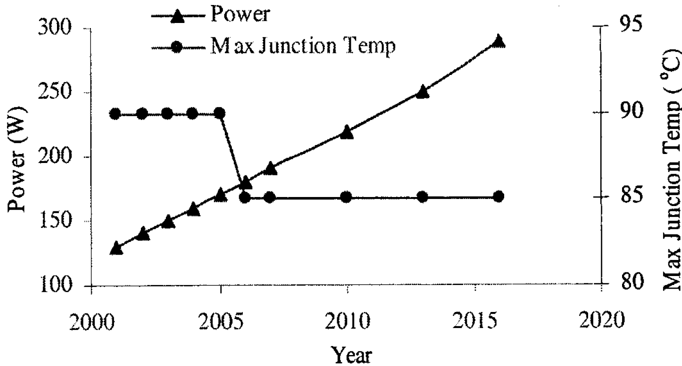


FIGURE 2 Power dissipation and maximum junction temperature in IC chips.

temperature. When a certain upper critical temperature is reached, important parts of the device may cease to function. Furthermore, temperature cycles that result from switching on and off the device can also cause problems, even if the operating temperature does not hit the upper critical temperature. This leads to another problem, the reliability of the device. It has been further reported[6] that temperature cycling of more than 20°C with respect to the peak temperatures can increase the failure rate of a device by eightfold. There is therefore an additional challenge to the thermal manager: a need not only to dissipate heat from the device, but also to do it gradually.

Downloaded At: 16:14 21 January 2011

THERMAL INTERFACE MATERIALS

IC chips are packaged to provide protection for the intricate circuitry within. There are many layers in a packaged chip, with every layer performing crucial roles is ensuring proper functioning of the chip. Figure 3 is a schematic, not drawn to scale, of typical packaged IC chip.

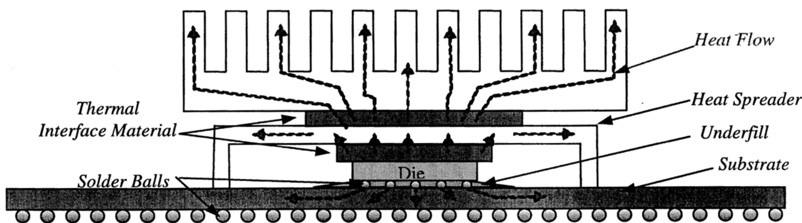


FIGURE 3 Schematic diagram of a packaged chip.

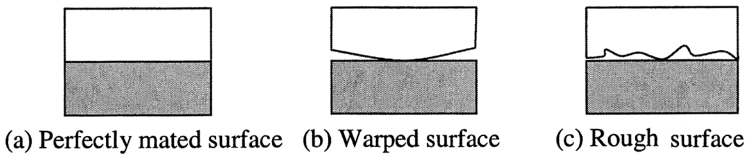


FIGURE 4 Schematic diagram of surfaces.

When the chip is powered up, the die gets hot and heat must be transferred out effectively to prevent overheating. Heat spreaders are incorporated to aid the spreading of heat from the small die to the big heat sink and eventually to the ambient air. Improvements on substrates and heat sinks, which are the junction of the actual IC and the ambient, can constructively affect thermal dissipation. It is of equal advantage to improve the interfacial heat path to the heat sink. The layers in the package create more interfaces for the heat to pass, and these solid interfaces become the bottleneck of the heat transfer. Solid surfaces, not being atomically smooth and straight, may be warped and rough. Figure 4 shows how three different surfaces are in contact with an atomically smooth surface.

As seen, the warped and rough surfaces that are common in the surfaces used in IC package create pockets of air trapped in the interface. These poorly mated surfaces cause a rise in contact resistance. There will be a temperature drop across the interface as a result of the impedance, as illustrated in Figure 5.

In IC packages today, thermal interface materials (TIM) are utilized to fill up the micro air voids, as seen in Figure 6. The conductivity of the thermal interface is not the only deliberation because the ability of these

Downloaded At: 16:14 21 January 2011

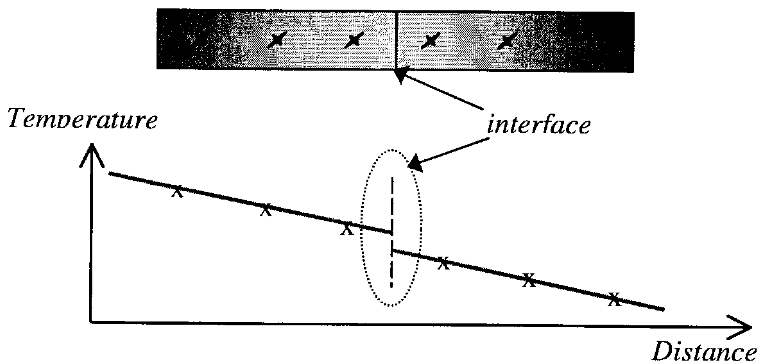


FIGURE 5 Temperature profile of two solids in contact.

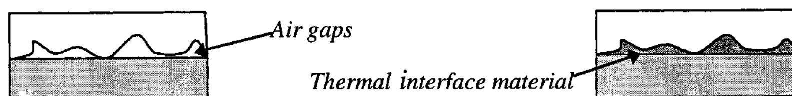


FIGURE 6 Utilizing thermal interface material to fill air voids.

materials to conform to the micro roughness at the interfaces is just as essential. Filling of the micro voids with thermal interface material will maximize the heat flow path and minimize thermal contact resistance. The use of a solid, for instance, copper, is therefore not a feasible choice for a TIM. Commonly used TIMs, in the semiconductor industry include thermal grease, polymeric adhesives, and phase change materials (PCM)[7]. PCMs have, in a majority of cases, replaced grease[8,9] because they are cleaner to use and provide much greater resistence to the liquid state being pumped out of the interface.

The polymeric TIM used in this study is based on a PCM manufactured by Honeywell Electronic Materials[10,11] that is described as a compliant and crosslinkable thermal interface material that comes in a dispensable liquid paste and elastomer film. Also described in the patents are methods to improve thermal conductivity of the polymer system. The material is, in principle, composed of paraffin wax, liquid rubbers, conductive fillers, and some additives. PCM absorbs latent heat to melt and release energy when it solidifies. The absorption and release of heat thus reduces the temperature cycling in its applications. These properties make PCM an important thermal interface material.

Downloaded At: 16:14 21 January 2011

EXPERIMENTAL

DSC and TGA Analyses

Thermal characterization on the TIM was carried out using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

The amount of weight loss at elevated temperatures measured using TGA (TA Instruments SDT2960 Simultaneous DTA-TGA) is useful to understand the thermal stability of the material. Significant weight losses at temperatures to which the material is normally subjected in processes and in applications can affect its bulk and interfacial thermal performance. In a typical measurement, 20–30 mg of PCM was placed in a ceramic pan and heated from room temperature to 500°C at 10°C/min in nitrogen purge.

DSC, in comparison, determines the amount of enthalpy change in a substance with temperature as well as its specific heat capacity (TA Instruments 2920 Differential Scanning Calorimeter with modulated

temperature capability). The temperature range of melting can also be elucidated. Enthalpy measurements were done with 20–30 mg of PCM in an aluminum pan and heated to 100°C to 10°C/min. Specific heat measurements were carried out after the system has been calibrated with a sapphire standard, with 20–30 mg of PCM in aluminum pans and heated at 5°C/min with a modulation +/− 1.00°C every 60 s. All measurements were done in nitrogen purge.

Thermal Resistance Measurements

Another technique utilized to characterize the material is the thermal resistance measurement. Thermal resistance and contact resistance measure how well heat is conducted. Thermal conductivity of homogeneous materials is independent of physical dimensions, while thermal resistance and contact resistance are very much dependent on the physical dimensions of the material. Thermal resistance[12] is the temperature gradient caused by a unit of heat flow through a material of a given size. From Fourier's Law of Conduction,

$$\theta = \frac{\Delta T}{q} = \frac{L}{k}.A \tag{1}$$

where θ = thermal resistance, ΔT = temperature gradient, q = amount of heat transferred, A = cross-*sectional area of material*, k = thermal conductivity of the material, and L = length of the material.

There is no commercial setup available in the market that satisfies this requirement. A setup was thus built and developed, using ASTM D5470-95 as guidelines. The American Society for Testing and Materials (ASTM) methods have very stringent requirements to suppress contact resistance contributions to the measured values. The ASTM D5470 standard requires a contact force of 435 psi. This value is very high compared to the typical pressure (less than 50 psi) used in the semiconductor packaging process. The surface smoothness requirement for the ASTM method is also very stringent. The contact surfaces have to be smoothly finished to within 0.4 μm (0.016 mils). A reasonably accepted smoothness by the industry for the surfaces is below 25.4 μm (1 mil). The experimental methodology has been used in a number of studies[13–18], and it involves sandwiching the material of interest with metal blocks and measuring the temperature drops across the metal blocks. Because of the sandwiching of the TM, contact resistance becomes a crucial issue. It can be anticipated to have a sizeable influence on the measured thermal resistance.

The thermal resistance measurement setup consists primarily of a test stand, two intermediate blocks, a temperature and a pressure control system, and a data acquisition system. A schematic diagram, not drawn

Downloaded At: 16:14 21 January 2011

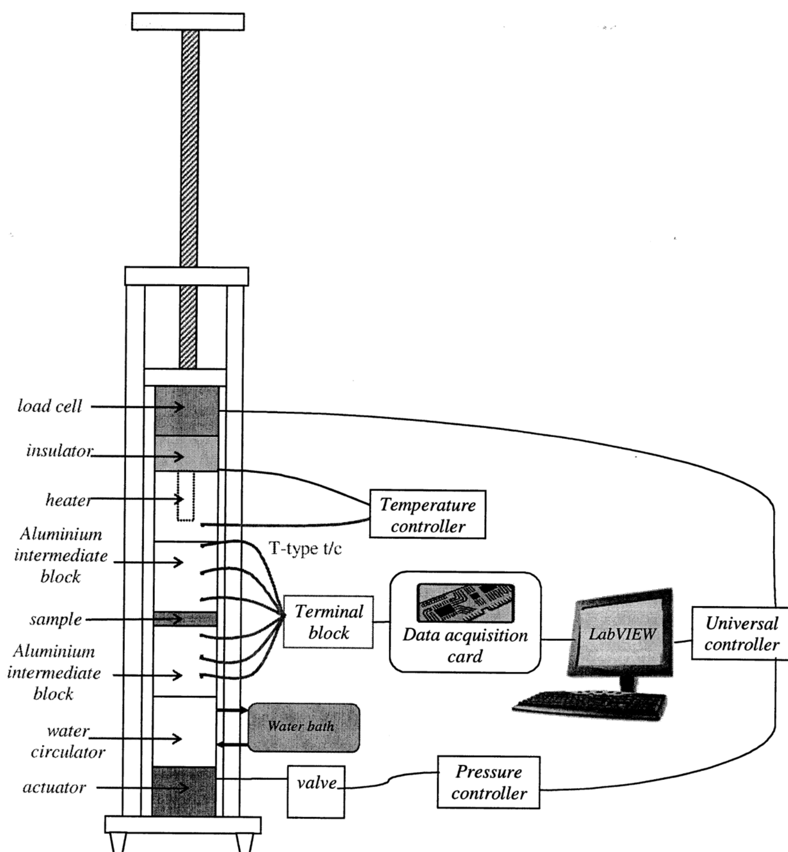


FIGURE 7 Schematic of the thermal resistance measurement setup.

Downloaded At: 16:14 21 January 2011

to scale, of the setup is as shown in Figure 7. The test stand is made of stainless steel. There is an opening in the test stand to insert the intermediate blocks. The size of the opening is determined by the extent of screw length after the different blocks and sample are assembled. The temperature control system is made up of an aluminum heater jacket to house a 200 W cartridge heater and a water cooler jacket that is connected to an 8005 Polyscience water circulator. A Teflon jacket to prevent excessive heat loss insulates the heater jacket. Type-T thermocouples with 0.6 mm diameter and accuracy of $\pm 0.1°C$ are used to monitor the temperature of the heater. A 2132 Eurotherm Controls temperature controller regulates the cartridge heater with reference to a thermocouple. The pressure applied on the stack is monitored using a Honeywall

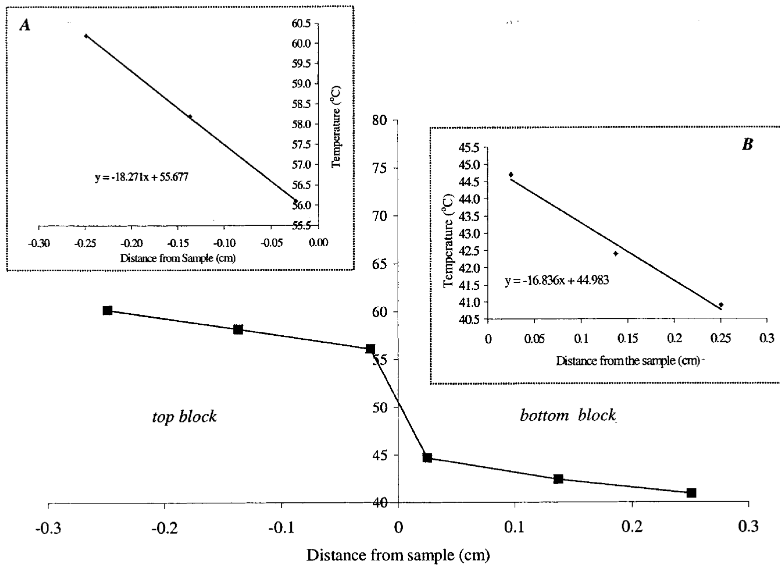


FIGURE 8 Graph of temperature drop across the intermediate blocks.

Downloaded At: 16:14 21 January 2011

universal controller, UDC 1000, via a Data Instruments SC500 load cell. The application of pressure can be done via the manual screw press or automatically using the actuator.

Three temperature measurements are taken at each aluminum block. Figure 8 is an example of the temperature profile that can be obtained.

As soon as the cartridge heater is switched on, a temperature junction within the intermediate blocks occurs. The interface material gets heated and cooled by the aluminum blocks above and below it respectively. The thermal resistance value can then be calculated using the following equation:

$$\theta = \Delta T/q \tag{2}$$

where θ = thermal resistance of interface material, ΔT = temperature drop across the sample (difference in the two intercepts A and B, and q = amount of heat transferred to the sample.

The amount of heat, q, transferred to the interface is calculated from the equation

$$q = K_{Al}A_{Al}\frac{\Delta T_{blk}}{\Delta x} \tag{3}$$

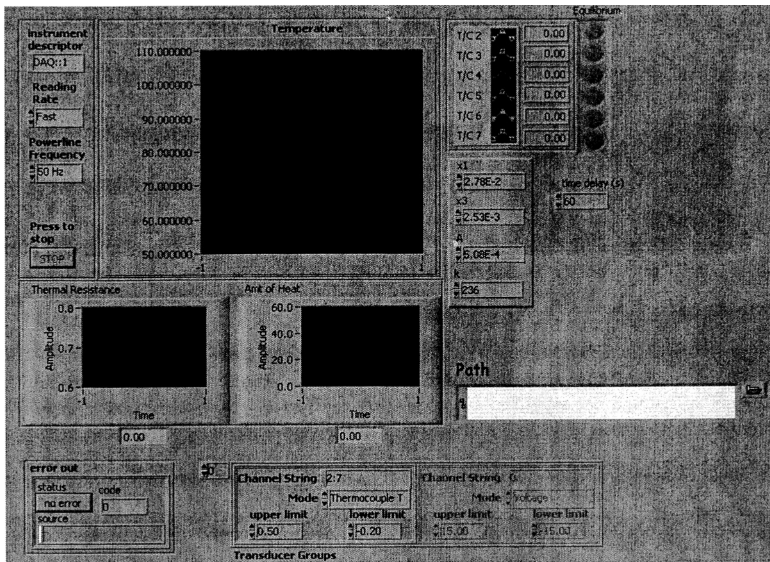


FIGURE 9 Front panel of programmed data acquisition software.

where k_{Al} = thermal conductivity of aluminum, A_{Al} = cross-*sectional* area of the aluminum block, and $\Delta T_{blk}/\Delta X$ = temperature gradient across the top aluminum block.

The temperature acquisitions are PC-assisted, via LabVIEW. The LabVIEW program is a virtual instrument and is made up of two components. The first one is the front panel (shown in Figure 9), which serves as the user interface. The other component is the block diagram, which contains the graphical source code that defines the tasking of the virtual instrument. The temperature readings from the six thermocouples are recorded and displayed in a waveform with digital indicators. The calculations for the thermal resistance measurement and the amount of heat supplied to the sample are displayed as the analyses proceed.

Every temperature data point from the analyses can be saved into a spreadsheet with the specified frequency. The temperature data were then processed using the LINEST function in a Microsoft Excel worksheet to calculate the exact amount of heat and the thermal resistance.

Thermal resistance and thermal conductivity of the TIM under study are measured using the described setup. The measurements are carried out to characterize the PCM-based TIM in simulations of its process and application conditions. The thermal conductivity of the PCM material was also determined from a least two measurements of thermal resistance at different thicknesses, but the same temperature and contact pressure.

Downloaded At: 16:14 21 January 2011

The commercial phase change material under study is in tape form of 10 mils thickness (2.54×10^{-4} m), and the thickness of the PCM was controlled using conductive spacers.

There are two ways in which the thickness of TIM can be controlled in the packaging process. One method is to use a use a spacer within the material, and the other is to use a particular pressure to adjust the thickness of the material. An experiment to simulate this process has been done. The test sample was prepared without the spacers in the material and was subjected to known pressures. The thermal resistance and the thickness were measured. TIM can be exposed to variable temperatures during both packaging process and applications, and it is important to understand the variations of its thermal properties as it is brought through a wide variety of thermal journeys. A fixed thickness of material was subjected to a constant contacting force and the thermal resistance was measured from sub-ambient temperature to 100°C.

RESULTS AND DISCUSSIONS

DSC and TGA Analyses

The TGA thermogram of PCM is shown in Figure 10. At an onset of about 150°C, PCM loses weight, with the highest rate of loss taking place at around 470°C. The PCM is a metal-filled polymer, and at 500°C almost all organics would have been lost and the weight of the sample reaches a plateau. From the thermogram, 13% of the total mass is left, indicating that the filler loading in PCM is about 87% by weight. The thermal

Downloaded At: 16:14 21 January 2011

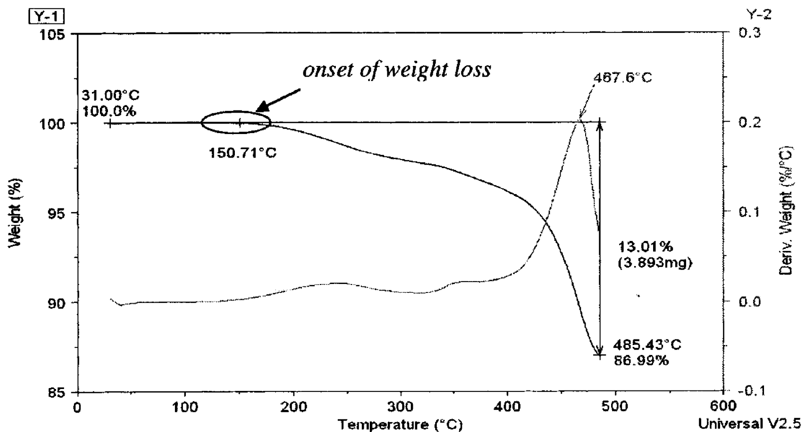


FIGURE 10 TGA thermogram of PCM.

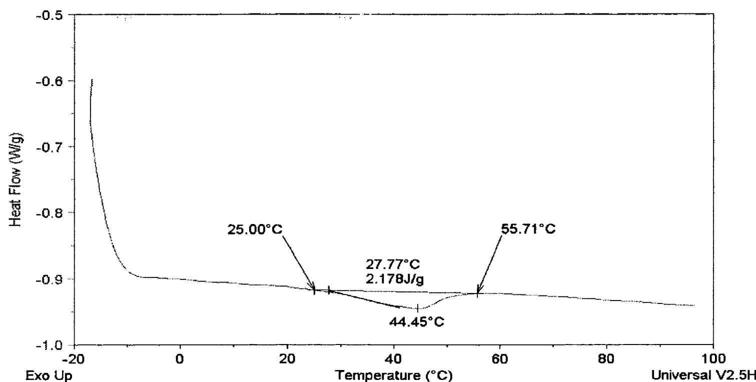


FIGURE 11 DSC thermogram of PCM.

Downloaded At: 16:14 21 January 2011

analysis also shows that the material cannot be brought above 150°C in its processes and applications. Upon reaching this onset, material degradation will occur, and the thermal performance of the material will most likely be affected. This onset is well above the projected temperature (Figure 2) that the material will be subjected to in its applications.

The DSC thermogram of PCM is shown in Figure 11. It is apparent from the thermogram that the onset of melting is gradual. At temperatures lower than ambient, the PCM is already changing phase as indicated by the deviation from the baseline. This explains why the material is a soft and moldable at room temperature. The maximum rate of melting took place at temperatures ranging from 42° to 45°C. The phase change is an endothermic process, and about 2.2 J of energy was absorbed in the process. The melting behavior of the PCM can be determined by the shape of the melting dip. Gradual melting is reflected by the broad valley-like shape. This is consistent with the fact that the material is made up of amorphous polymer (rubber); melting of a highly oriented polymer yields a sharp melting onset and steep valley. The material is also of a single phase because of the absence of multiple dips. The glass transition temperature of PCM is below −20°C and is not reported here because it is much lower than the application temperatures.

The trend in specific heat capacity of PCM is shown in Figure 12. The specific heat capacity of the material is relatively constant over the tested temperature at values 1.0 to 1.1 J/g/°C, with a slight increase at the phase change region (40°–45°C) due to the absorption of energy. The specific heat capacity values are, however, comparable to the specific heat capacity of aluminum (0.9 J/g/°C), which makes up 87% of the material weight. The high percentage of aluminum has also resulted in the constant value of specific heat capacity with increasing temperature. This amount of heat absorbed by the material to give a unit rise in

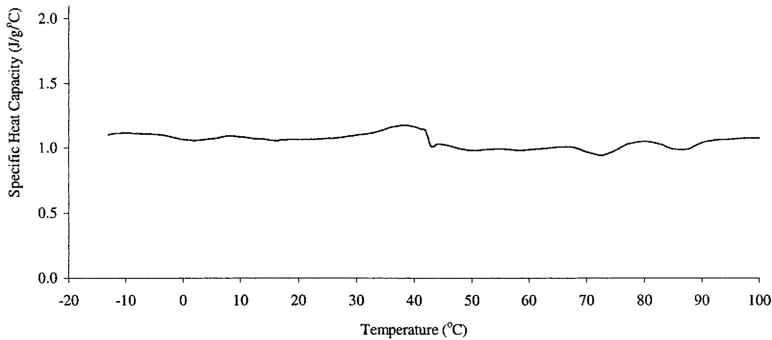


FIGURE 12 Specific heat capacity of PCM over temperature.

temperature is an important characteristic of the material. The higher this value is, the better the material will perform in real-life applications.

Thermal Resistance Measurements

Thermal conductivity results are shown in Figure 13. The thermal conductivity of the PCM material can be determined from at least two measurements of the thermal resistance of different PCM thicknesses at the same temperature and contact pressure. Thermal impedance is the product of thermal resistance and the cross-sectional area. From Equation (1), the reciprocal of the thermal resistance versus thickness plot will yield the thermal conductivity of the material of interest.

$$\theta . \mathrm{A} = \frac{L}{k} \tag{4}$$

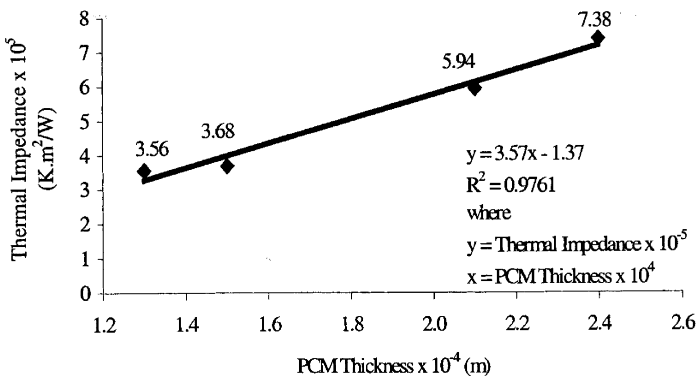


FIGURE 13 Graph of thermal impedance of PCM vs. thickness.

Downloaded At: 16:14 21 January 2011

where θ. A = product of thermal resistance and cross-sectional area = thermal impedance, k = thermal conductivity, and L = length of the material.

The commercial phase change material under study is in tape form of 10 mil thickness (2.54×10^{-4} m). The thickness of the PCM was controlled using conductive spacers. The resultant measurements are shown in Figure 13.

The measured thermal conductivity is the reciprocal of its slope. From Figure 13, the measured thermal conductivity of PCM is 2.8 W/mK. This measured value is close (within 10% of accepted error range) to the reported value of 3.0[19]. The contact resistance of the material to interface is impedance at zero thickness and is 1.37×10^{-5} Km^2/W.

The effect of variation in pressure on the performance of the material is shown in Figures 14 and 15. The pressure tested in this experiment covered the typical 0.14–0.35 Mpa pressure range used in packaging processes. From Figure 14, it can be seen that the thickness of PCM settles down to 0.05 mm when subjected to a pressure of at least 0.14 Mpa. This pressure is a typical value used in packaging processes in the industry. The maximum pressure used in the industry can be as high as 0.35 Mpa. As per Equation (1), it can be seen that thermal resistance is directly proportional to the thickness of the sample. The corresponding thermal resistance is, therefore, directly reflected by the trend in the thickness of PCM. As observed Figure 15, optimized thermal performance can be achieved with at least 0.18 Mpa of pressure.

The device temperature in which PCM operates can vary remarkably. When the device has just started working the PCM is at room temperature, but over time the temperature can go beyond 100°C. The maximum rate at which PCM is changing phase is approximately 45°C

Downloaded At: 16:14 21 January 2011

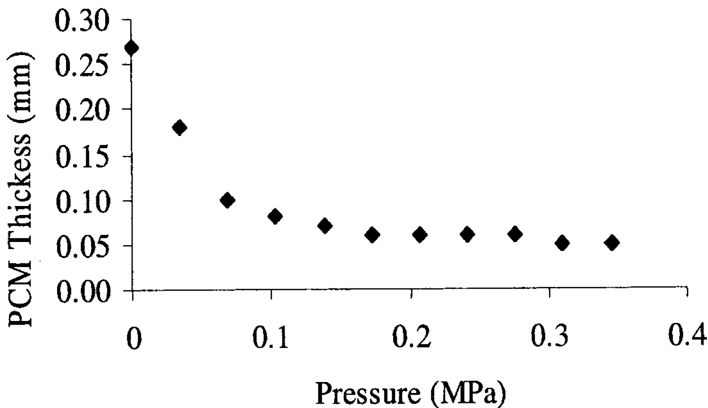


FIGURE 14 Graph of PCM thickness with increasing pressure.

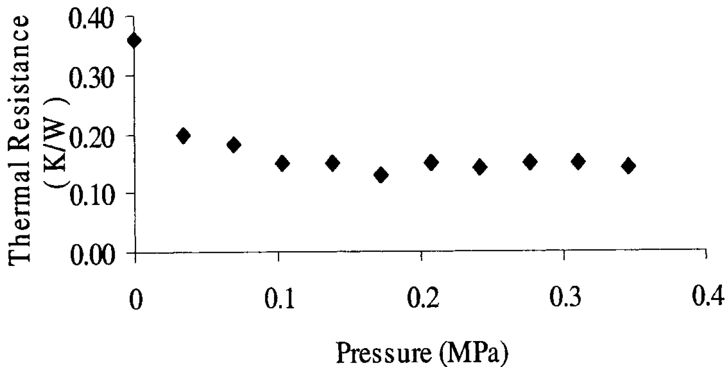


FIGURE 15 Graph of thermal resistance of PCM with increasing pressure.

Downloaded At: 16:14 21 January 2011

(referring to Figure 11), and the conformance of the material on a metal surface should therefore be greatly improved. This trend is clear from the thermal resistance measured over temperature (while maintaining constant contact pressure) shown in Figure 16.

The thermal resistance was expected to decrease with increasing temperature (after melting) due to the increase in the extent of molecular vibrations. This effect, however, is not apparent in the results obtained. In view of Figure 17, the change in temperature has evidently increased the amount of heat transferred to the sample, but these increases were accompanied by increases in the temperature drop across the sample. This leads to the resultant measured thermal resistance being constant temperature as seen in Figure 16.

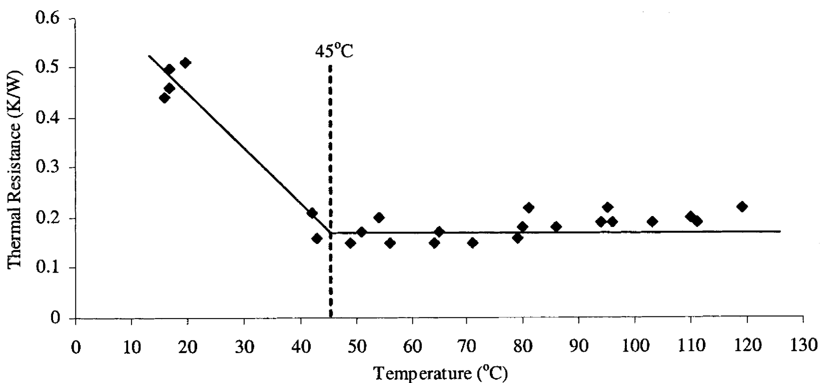


FIGURE 16 Graph of thermal resistance of PCM over temperature.

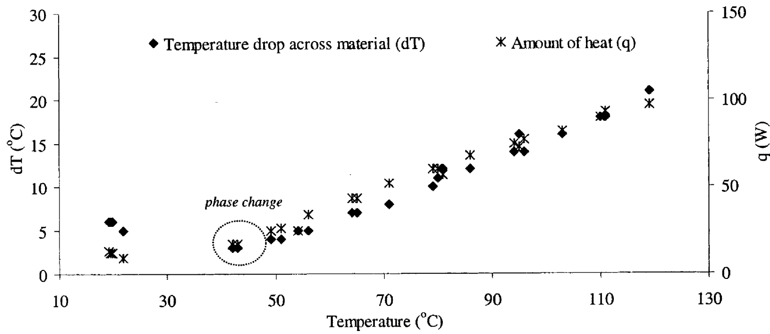


FIGURE 17 Graph of temperature drop across and amount of heat transferred to PCM over temperature.

CONCLUSIONS

The physical properties of phase change material (PCM) have been analyzed for its application as a thermal interface material. The melting enthalpy and specific heat capacity are 2.2 J/g and 1.0–1.2 J/g/°C respectively. It starts to lose weight when brought to temperatures above 150°C until all its 13% organic components are lost. The ability of the material to conform to metal surfaces and allow transfer of heat has been elucidated with the measurement of thermal resistance. The setup to measure thermal resistance was designed and built using ASTM D5470 as guidelines. The thermal conductivity of the material was measured using the setup and found to be in good agreement with the reported 3 W/mK value. Effects of packaging processes and application conditions like temperature and pressure were investigated and minimum pressure of 0.14 Mpa (15 psi) was enough for the material to reach its minimum thermal resistance. The temperature of the device (if it does not go beyond 150°C) will not affect the thermal performance of the material.

Downloaded At: 16:14 21 January 2011

REFERENCES

[1] Ameen, J., R. M. Miller, and P. V. Yokimens. (1998). Dealing with the heat. IEEG *Circuits & Deivces*, pp. 38–40.
[2] http://www.intel.com
[3] International Technology Roadmap for Semiconductors 2000, http://public.itrs.nte/
[4] International Technology Roadmap for Semiconductors 2001, http://public.itrs.nte/
[5] International Technology Roadmap for Semiconductors 2002, http://public.itrs.nte/
[6] Bar-Cohen, A. and A. D. Kraus. (1983). *Thermal Analysis and Control of Electronic Equipment*. Washington, D.C.: Hemisphere, Ch. 1, 4, 9.

[7] Kranz, R. (2000). Thermal interface materials for high-power BGAs, *Adv. Packag.*, pp. 29–32.

[8] Debabrata, P. (1996). Application of Phase Change Materials To Passive Thermal Control of Electronic Components. Ph.D Thesis – University of Maryland at College Park. Ann Arbor, MI: University Microfilms International, pp. 1–26.

[9] Chiu, C. P., B. Chandran, M. Mello, and K. Kelley. (2001). An accelerated reliability test method to predict thermal grease pump-out in flip-chip application. In *Proceedings of the 2001 Electronic Components and Technology Conference*. New York: IEEE.

[10] Nguyen, M. N. and J. D. Grundy. (1999a). Compliant and Crosslinkable Thermal Interface Materials. U.S. Patent 5,989,459, March 9, 1999.

[11] Nguyen, M. N. and J. D. Grundy. (1999b). Compliant and Crosslinkable Thermal Interface Materials. U.S. Patent 6,238,596, September 17, 1999.

[12] A Brief Explanation of Spreading Resistance, http://www.engr.orst.edu/~petersr/hspread.html

[13] Aoki, R. and C. P. Chiu. (1998). A testing apparatus for thermal interface materials. In *Proceedings of the 1998 International Symposium on Microelectronics*. pp. 1063–1041.

[14] Solbrekken, G. L., C. P. Chiu, B. Byers, and D. Reichenbacher. (2000). The development of a tool to predict package level thermal interface material performance. In *2000 Intersociety Conference on Thermal Phenomena*. pp. 48–58.

[15] Rauch, B. (2000). Understanding the performance characterisation of phase-change thermal interface materials. In *2000 Intersociety Conference on Thermal Phenomena*. pp. 42–47.

[16] Dean, N. F. and A. Gupta. (2000). Characterisation of a thermal interface material for burn-in application. In *2000 Intersociety conference on Thermal Phenomena*. pp. 36–41.

[17] Kohli, P., M. Sobezak, J. Bowin, and M. Matthews. (2001). Advanced thermal interface materials for enhanced flip chip BGA. In *proceedings of the 2001 Electronic Components Technology Conference*. New york: IEEE.

[18] Rauch, B. (1999). Test methods for characterising the thermal transmission properties of phase-change thermal interface materials. In *Electronics Cooling*, Vol. 5, No. 2, pp. 16–20.

[19] http://www.electronicmaterials.com/products_services/packaging/thermal_interface_solutions.html

Downloaded At: 16:14 21 January 2011