Nanofluids, Nanogels and Nanopastes for Electronic Packaging

Rabindra N. Das, Varaprasad Calmidi, Mark D. Poliks and Voya R. Markovich
Endicott Interconnect Technologies, Inc., 1093 Clark Street, Endicott, New York, 13760.
Telephone No: 607-755-1389, E-mail: rabindra.das@eitny.com

Abstract

This paper discusses polymer based nanogels, nanofluids and nanopastes for thermal interface material (TIM) applications. Nanopaste and nanogel formulated using controlled-sized particles to fill small bond lines is highlighted. A variety of nanopaste with particle sizes ranging from 5 nm to 15 μm was bonded between metal plates. SEM and optical microscopy were used to investigate the micro-structures, conducting mechanism and path. Thermal impedance decreased with increasing curing temperature. It was found that with increasing curing temperature of the paste, the thermal impedance decreased due to sintering of metal particles. Paste modified with nanoparticles showed 30-90% thermal impedance drop when cured at 275 °C instead of 200 °C. Paste formulated with a low melting point (LMP) filler exhibited a thermal impedance as low as 48 mm^2 C/W. The paper also describes a nanoparticle dispersion approach to prepare nanogels and nanofluids. Several nanogels were tested in a thin bond line construction as thermal interface materials. Here we highlight recent developments on nanogels. The content of nanoparticles in the gels ranged from 4 % to 20 % by weight. Materials exhibited viscosities as high as 1000 Pa s for gels, and as low as 200 Pa s for low flow liquid like materials. Similarly, viscosities for oils and solvent based fluids were 500 cp and 10 cp respectively. Stability of nanoparticles with in the gel was ascertained by thermal treatments. The thermal performance of gels was characterized using thermal impedance measurements. The thermal impedance of gel, liquid like materials and oil based fluids were in the range of 70-75, 46-52 and 53-65 mm^2 C/W respectively. The present processes and materials allow fabrication of robust thinner bondline TIM structures.

1. Introduction

Nanofluids have received much attention due to their novel electronic, magnetic, optical, thermal, and biological properties [1-3]. Nanofluids are formed when nano particles are dispersed in a base fluid. Depending on the size of particles and dispersing medium, one can generate a range of functional fluids. For example, nanoparticle – aqueous ethylene glycol (EG) based nanofluids are proposed as the next generation heat transfer fluids because of their significantly higher thermal transport capacities compare to the base liquids [4-5]. In parallel significant research work has focused on nanopastes for Z-axis interconnections [6,7], die attachments and thermal interface materials (TIM). Nanogels have the potential to combine the advantages of both nanofluids and nanopastes. The combination of high thermal conductivity and stability makes nanogels very attractive candidates for TIM. Nanopastes and nanogels are widely pursued since they offer numerous advantages in terms of ease of processing, good compatibility with a variety of substrates, and great opportunity for structural modifications. A number of nanoparticle pastes, fluids including carbon-ethylene glycol, metal-epoxy, and metal-silicone have been developed. For example, Xiao et al [8] describes epoxy or silicone based conductive adhesive joints and their thermal and mechanical stabilities. Jeong et al [9] reported the effect of curing behaviors, solvent evaporation and shrink, on conductivity of adhesives. They [10] also described conductivity of micro filled adhesives upon addition of nanoparticles. Lee [11] reported on the addition of nano-sized silver particles to micro-sized flakes, and the effect on resistivity for these mixed-sized silver particle-filled conductive adhesives. Goh et al [12] mentioned the effect of annealing on the morphologies and conductivities of sub-micrometer sized nickel particles used for electrically conductive adhesive. Inoue et al [13] investigated the variations in electrical properties of a typical isotropic conductive adhesive (ICA) made with an epoxy-based binder that are caused by differences in the curing conditions. Coughlan et al [14] described electrical and mechanical analysis of conductive adhesives where the main properties of joint resistance and adhesive strength were examined before and after different environmental treatments. Bourlinos [15] described silica and ironoxide based nanosalts with liquid like behavior. Sancakter et al [16] reported pressure-dependent conduction behavior with particles of different sizes, shapes, and types. The effects of external pressure on the filler resistance were measured. Jiang et al [17] reported on surface functionalized nano silver-filled conductive adhesives. Li [18] reported well-dispersed Self-assembled silver nanoparticles for preparing oil based nanofluids. Although several nanofluids and nanopastes are available, it appears that there is still scope for new approaches leading to less complicated, more versatile and inexpensive methods to produce new structures and enable better control over the electrical and thermal properties.

In the present study, nanogels and nanopastes formulated using nanoparticles, ranging from 5-100 nm, were used to fabricate thermal interface materials for microelectronics. Motivated by the extraordinary performance of nanostructures in nanocomposites design, we search for inorganic nanoparticles that by dispersion in an appropriate organic matrix can display similar multi-functional qualities in the nanometer length scale. We found few good candidates among nanogels for thermal interface materials. However accommodation of these advantages into TIM applications requires a collective analysis of both heat transfer as well as gelation properties. Nanoparticles increase overall thermal conductivity, whereas the polymer matrix provides better processability and mechanical robustness. However, homogeneous dispersion of nanoparticles in the polymer gel matrix is a critical step in order to achieve high quality gels.

2. Experimental Procedure

A variety of silver, copper, and low melting point (LMP) filler based nano and micro particles and their dispersion into polymer matrix were investigated in order to achieve uniform mixing in the adhesive or gel.   In a typical procedure, polymer-based conductive adhesives were prepared by mixing appropriate amounts of the conducting filler powders and epoxy resin in an organic solvent to form a paste like composition. For thermal conductivity measurements, a thin film of this paste was deposited between two metal plates and cured at different temperatures ranging from 150 °C to 285 °C. Adhesives were characterized by Scanning Electron Microscopy (SEM) and infrared microscopy to ascertain sintering and thermal behavior. A Keithley micro-ohmmeter was used for electrical measurements.
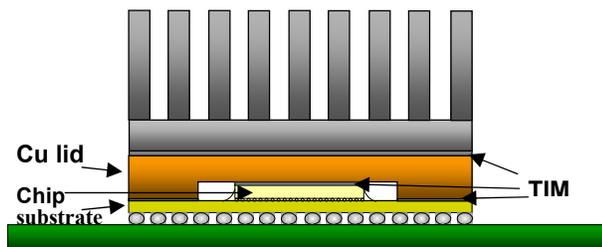
**Figure 1:** Schematic of a high performance organic flip-chip BGA package on a PWB.

3.1. Thermal interface materials (TIM)

Thermal interface materials (TIM) are critical packaging materials that are intended to fill gaps between mating surfaces to enable efficient heat transfer. TIM are used in a variety of forms like silicone and epoxy adhesives, gels, greases, phase change materials, and metal alloys like solders.   **Figure 1** shows a schematic of a typical high performance organic flip-chip BGA package on a PWB. In this figure, three different applications of TIM are shown. For high performance applications, the TIM between the chip and copper lid is usually the critical interface because it is in the primary heat flow path and due to the relatively small area of the chip compared to that of the package. The TIM between the package and the heatsink provides thermal contact between the package and the heatsink.   The third location for the TIM is between the copper lid and the substrate. This interface is usually not as critical as the other two instances. However, being a structural interface, it will need to have good adhesion properties in addition to being able to conduct heat down into the PWB if needed. [**19**]. In general, organic packages benefit from low stress TIM like gels, greases and pastes since they are stress decoupling in nature and tend to increase package reliability. However, in some cases, TIM with adhesive properties can be used to control warpage and strain improving package reliability as well.
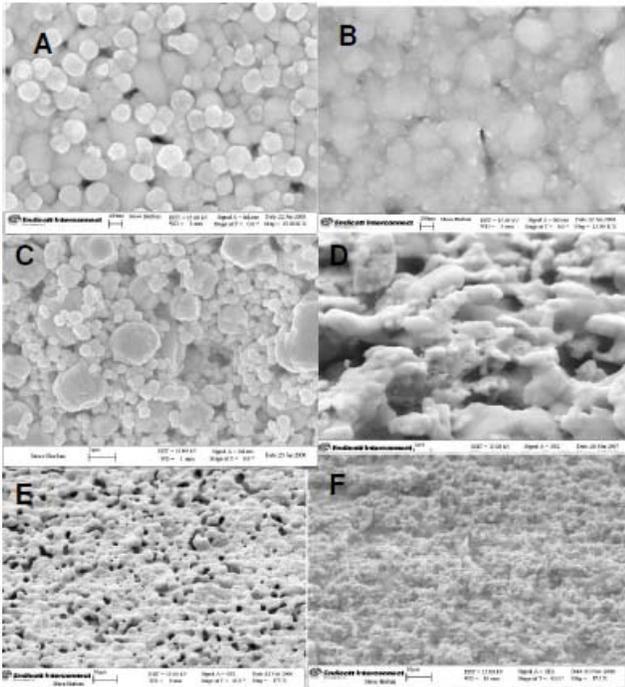
3.2. Nano-Paste

A conductive paste is a composite material consisting of a nonconductive polymer binder and conductive filler particles. When the filler content is high enough, the system is transformed into a good electrical and thermal conductor. The formation of a conduction path was observed by optical and SEM images of sample cross sections. **Figure 2A** shows a cross section of a LMP-based paste.   LMP melts and produces a continuous metallic network. In the silver adhesive, the average filler diameter is in the range of 5 μm. Filler loading was high and adjacent particles united mutually and necking phenomena between fillers occurred; namely, a conduction path was achieved, as shown in **Figure 2B**. A variety of silver filled adhesives with a mixture of nano and micro particles were studied. In nano-micro mixtures, nano particles occupy interstitial positions to improve particle-particle contact for conductivity. For the silver nano particles, the fillers can self sinter and make a continuous conduction path. **Figure 2C** represents micro structures of nano-micro silver filled pastes.
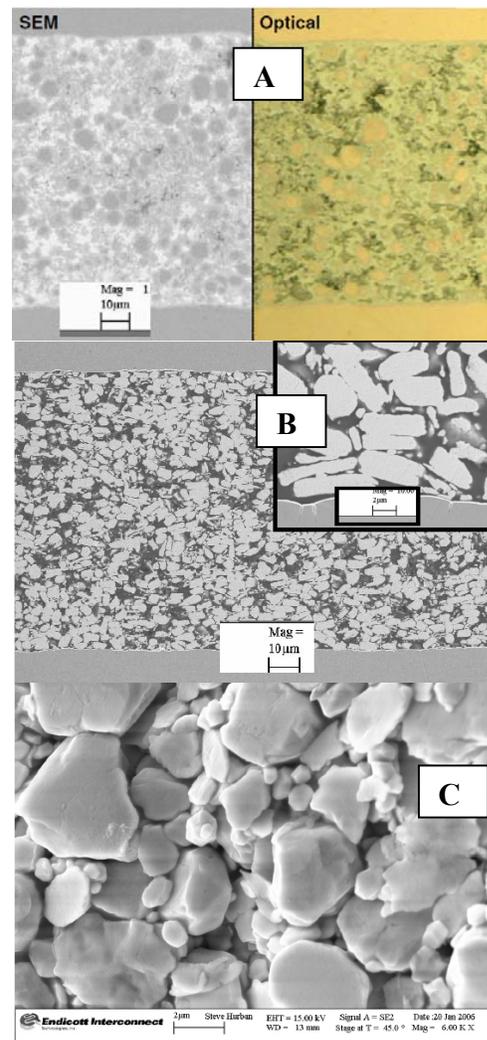

Figure 2: SEM and optical micrographs of adhesives; (A) low melting point (LMP) alloys (left side SEM and right optical photograph), (B) SEM of silver micro particles and inset has higher magnification, and (C) mixture of silver nano and micro particles.

Figure 3: SEM micrographs for the nanoparticle sintering (A) 100 °C, (B) 200 °C. SEM micrographs for the nano-micro filled silver based conducting adhesives; (C) un-sintered, (D)-(E) sintered, and (F) LMP based sintered conducting pastes.

3.2.1. Sintering

It is well known that change in grain size has a direct impact on the electronic properties of a system. In view of this, a systematic investigation of electrical resistance behavior of silver nano and nano-microcomposites has been carried out, and the results of such an investigation are presented here. Sintering temperature can be greatly reduced when the size of particles is decreased to 10-15 nanometers. Due to the decrease of size, diffusion and growth of the nanoparticles is much easier, and large grains (hundreds/thousand of nanometers) can be produced efficiently. These nanoparticles diffuse with each other and are gradually sintered by neck-formation (**Figure 3A-B**) between the adjacent particles during the thermal anneal process on the substrate. The neck can be smoothed away gradually. The grains of nanoparticles convert into a continuous surface. In the nano-micro composites, the main components are a mixture of nanoparticles and microparticles. The nanoparticles may contact with the adjacent ones, but the nano aggregation lengths are short, less than 10-fold of the microparticle diameter on average (**Figure 3**). As the sintering temperature increases, particle diffusion becomes more and more obvious. The aggregation length becomes much longer, resulting in the formation of one-dimensional jointed particle assemblies developing into a smooth continuous network (**Figures 3D-E**).
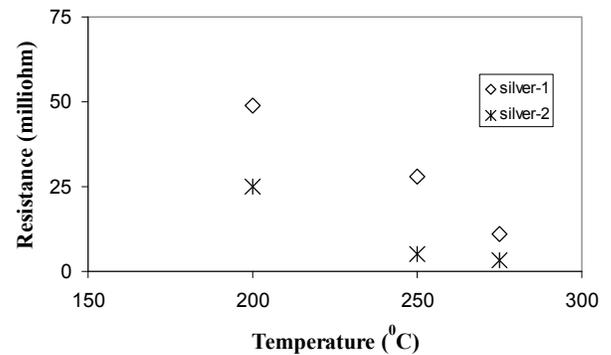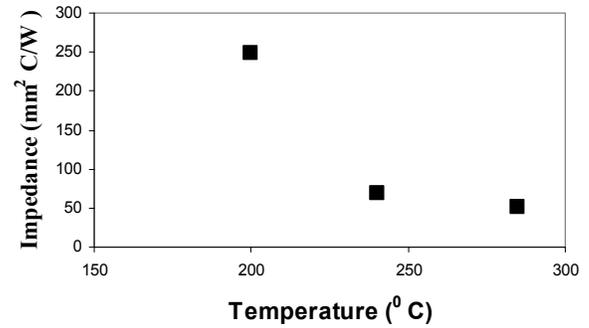

Figure 4: **(A)** Thermal Impedance and **(B)** Resistance as a function of temperature for silver-based nano-micro pastes.

Conducting pastes cured at 200-275 °C showed low thermal impedance. Impedance decreases with increasing curing temperature due to sintering of metal particles. **Figure 4A** shows impedance of nano-micro silver paste as a function of curing temperature. There is a significant impedance drop with increasing curing temperature from 200 °C to 275 °C. Thermal impedance of 15nm based nano-micro paste sintered at 240°C and 275 °C are 69 mm^2 C/W and 52 mm^2 C/W, respectively. Above 200 °C, particle sintering plays an important role to maintain low impedance. All adhesives fabricated from low melting point (LMP) filler based paste showed low impedance even at lower curing temperature, whereas silver adhesives when curing below sintering temperature showed higher impedance. Silver nano-micro paste cured at 200 °C showed impedance in the range of 248 and the impedance decreased to 48 mm^2 C/W when LMP based pastes were used. **Figure 4B** shows electrical resistance of silver-based nano-micro conducting adhesives as a function of curing temperature. Electrical resistance and thermal impedance of nano-micro adhesives decreased with increasing curing temperature. Conductivity measurements show that the 10-50% nanoparticle containing paste showed around 80- 90% electrical resistance and thermal impedance drop when cured at 275 °C instead of 200 °C.
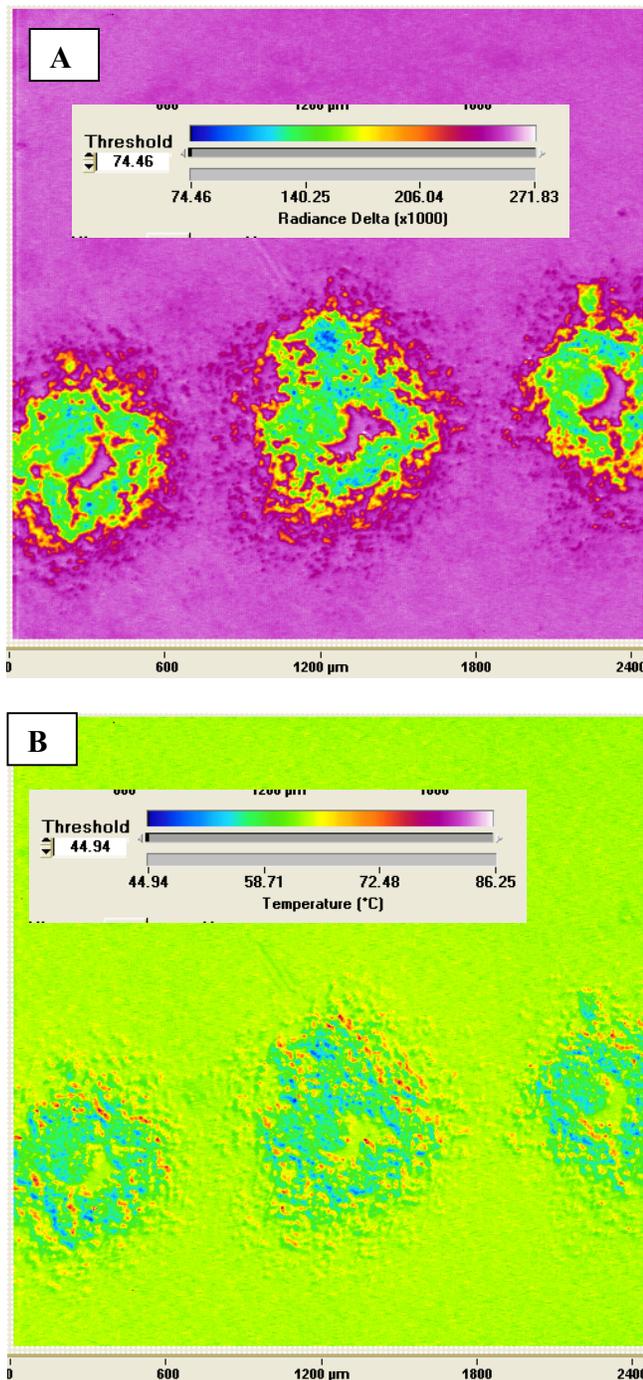
3.2.2. IR Image of Sintered and Un-sintered Paste

To study the influence of sintering on the thermal radiance behavior, both sintered and un-sintered samples were characterized by infrared radiance image. Thermal conductivity and emissivity of materials will determine

radiance. For thermal conduction, particles should make intimate physical contact and form a network (conductive chain), which helps in transfer of heat. This conductive path is formed at a threshold volume fraction of conductive filler, which is a critical value at which all particles contact each other and form a conductive network in the resin. Emissivity is a surface phenomenon. Under thermal equilibrium, emissivity of materials will play a critical role for emitted radiance.
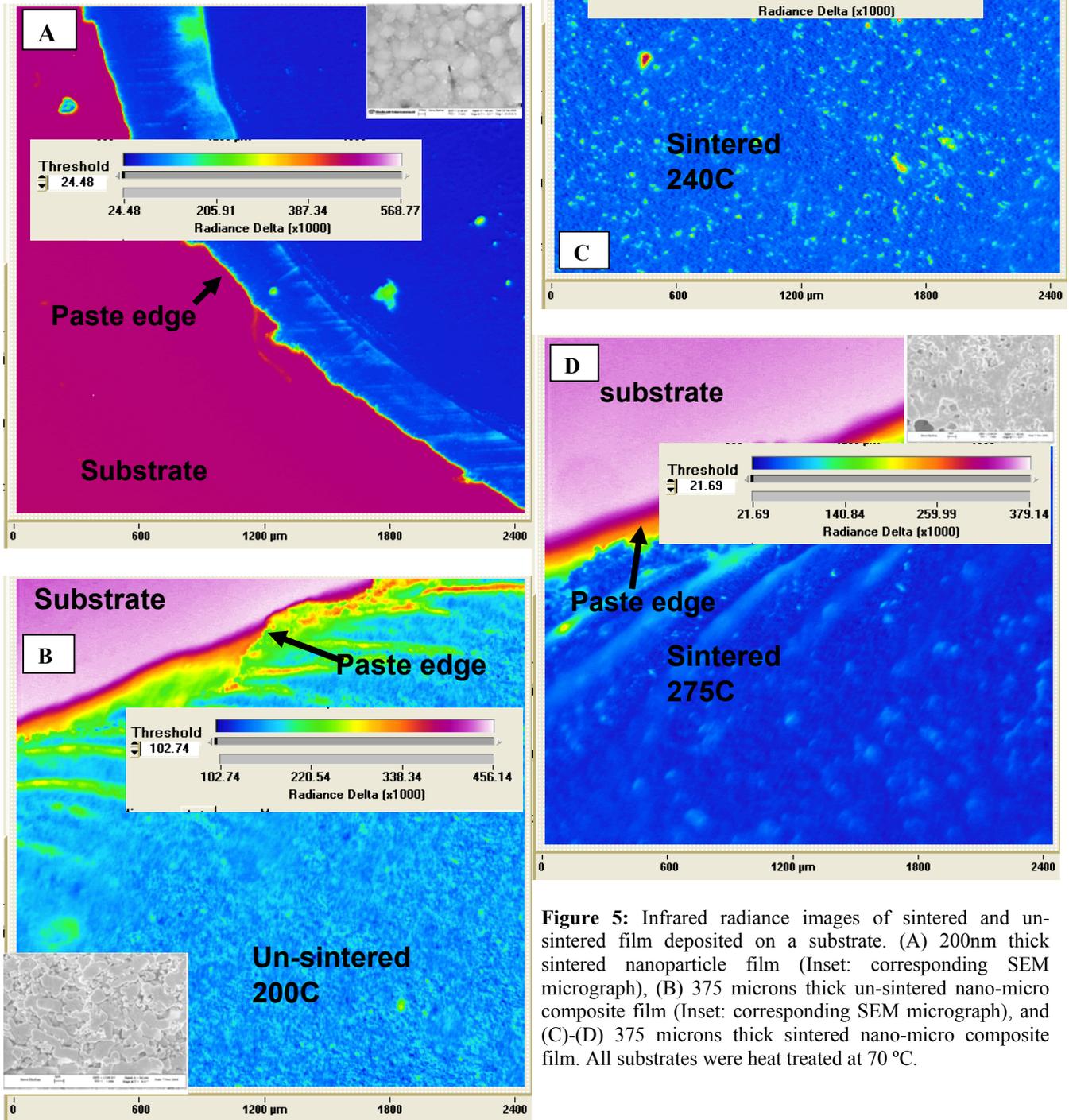
Figure 5: Infrared radiance images of sintered and un-sintered film deposited on a substrate. (A) 200nm thick sintered nanoparticle film (Inset: corresponding SEM micrograph), (B) 375 microns thick un-sintered nano-micro composite film (Inset: corresponding SEM micrograph), and (C)-(D) 375 microns thick sintered nano-micro composite film. All substrates were heat treated at 70 ºC.

Figure 6: IR images of paste filled substrate heat-treated at 65 ºC (A) radiance profile and (B) temperature profile.

Figure 5 represents the IR radiance image of 0.2 micron thick sintered silver nanoparticle film, 375 microns thick un-sintered and 375 micron thick sintered silver nano-micro composites. It is clear from the figure that all the samples radiate less energy than the base substrate. **Figure 5B** represents IR image of 375 microns thick unsintered nano-micro paste. The radiance level of low temperature heat-treated un-sintered paste will be higher than sintered paste. For sintered paste the radiance level was less. With further increase in sintering temperature, the heat transfer

phenomenon remains unchanged (**Figures 5C-D**). In fact, all the sintered films including thin nanoparticle film and thick nano-micro sintered composites shows a similar IR image as can be seen in **Figures 5A, C, and D**. Such an observation is obvious because particle inter-diffusion at the surface level will be equivalent and behaves more like a continuous metallic network for lower emissivity. The observation suggests that the heat-transfer/radiance mechanisms are the same for the sintered thin, thick nano or nano-micro composites. Based upon the images observed above, we suggest a heat/energy transfer mechanism for the sintered nano or nano-micro composites as follows. In the sintered film, nanoparticles are smaller and highly reactive due to immediate particle-to-particle contact. Moreover, the diffusion (sintering) distance of nanoparticles should be lower than that of the corresponding bulk solid. At or above sintering temeparture, the particles inter diffusion will generate a metallic network surface for low emissivity. For unsintered film (**Figure 5B**), the individual particle and polymer plays an important role for higher radiance. In this region, the exposed surface polymer is sufficient to increase emissivity of film.

Furthermore, we have investigated the thermal behavior of paste filled substrates. A few optimized metal-epoxy pastes were used for hole fill applications to fabricate z-axis interconnections in laminates. Conductive joints were formed during composite lamination using an electrically and thermally conductive adhesive. Z-axis interconnection was achieved using joining cores. Through holes in the joining cores, formed by laser or mechanical drilling and having diameters ranging from 50 μm to about 600 μm, were filled with an optimized conductive adhesive. The adhesive-filled joining cores were laminated with circuitized subcomposites to produce a composite structure. High temperature/pressure lamination was used to cure the adhesive in the composite and provide Z-interconnection between the circuitized subcomposites. A variety of joining core structures such as 0S/1P, 0S/2P, etc. were used for hole fill applications. The cores can be structured to contain a variety of arrangements of signal, voltage, and ground planes. In addition, signal, voltage, and ground features can reside on the same plane. By alternating 2S/1P and 0S/1P cores in the lay-up prior to lamination, the conductive paste electrically connects copper pads on the 2S/1P cores that reside on either side of the 0S/1P core. Two signal layers are added to the composite structure each time one adds an additional 2S/1P core and an additional 0S/1P core. IR image of a structure with 6 metal layers is shown in **Figure 6** as a representative example. IR image clearly distinguish paste area and dielectric area. Paste has various hot and cold spots. On the other hand, dielectric has uniform temperature/radiance distribution. In a typical paste filled system, the metal should form few continuous metallic network throughout the via. Red hot spots may be indicating that continuous metallic network. Blue or cold zones may indicate the unsintered zone.
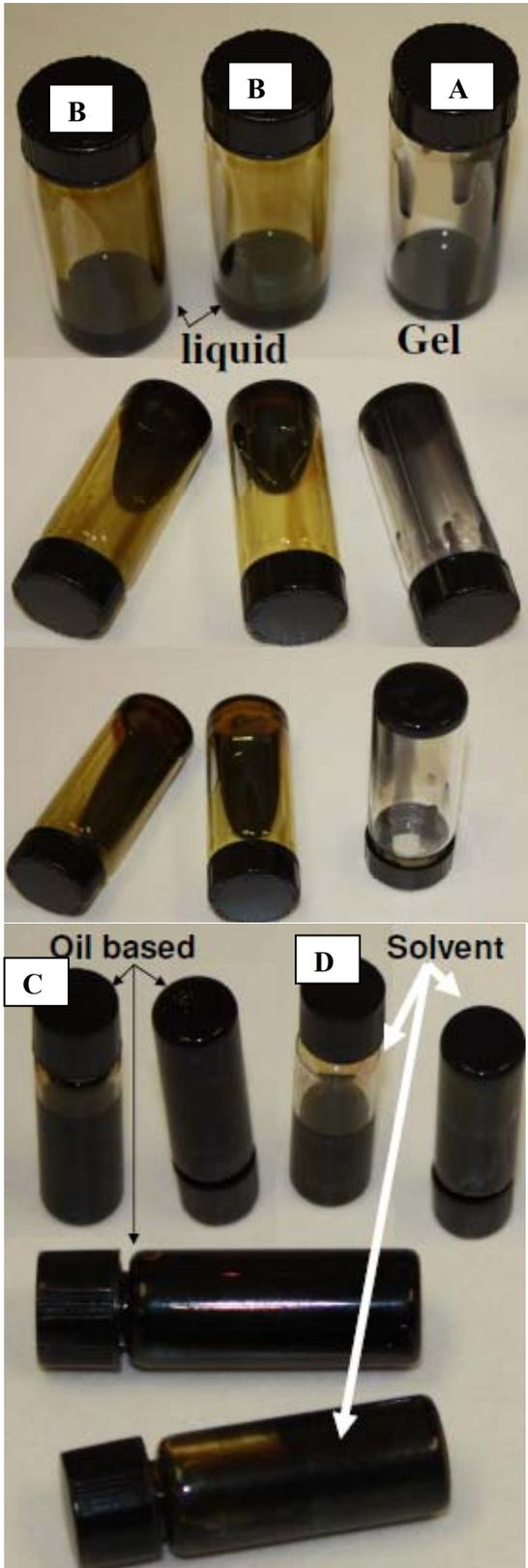
Figure 7 : Photographs and flow characteristics of (a) Nano-Gel, (B) liquid like materials, (C) Oil based nanofluids, and (D) solvent based Nanofluids.
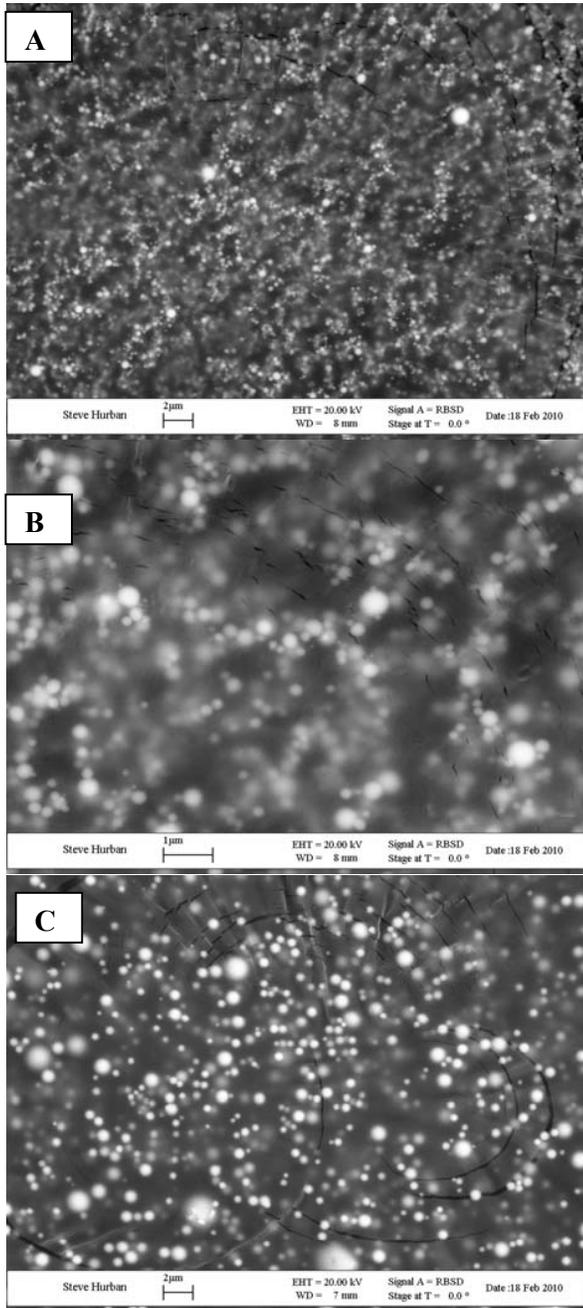
3.3. Nano-gel

Nano materials have potential applications at all levels of microelectronics. Nano TIM with desired properties and thickness present significant challenges. Nano paste, gel, liquid like materials, and fluids can be used for different TIM applications. **Figure 7** shows a series of nanogels and nanofluids. Nanogel is best performed with liquid like materials having low viscosity, in the range of 100-200 Pa s. Low viscosity helps generation of thin bond line. Nanopaste is best performed with similar viscosity pastes (100,000-300,000 cps), and generates ~50-100 micron thick bond lines. **Figure 7A-D** represents different viscosity nanogels and nanofluids. Lower viscosity can produce low flow liquid like materials. Bondline can be reduced further for oil based nanofluids.

To date, development of new generation ambient TIM has been based almost exclusively on uncured highly filled pastes. One of the major challenges in these systems is to decrease bond line and decrease the thermal impedance. Larger particle size makes the system even more challenging. Nanogel TIM, on the other hand, synthesized by incorporating nanoparticles into a polymer gel matrix, combines the high thermal conductivity with the excellent thermal stability toward high temperature application. Nanogel TIM combine the advantages of both paste and nanofluids. The nanogels are prepared by adding 5-10 nm silver within a polymer matrix.
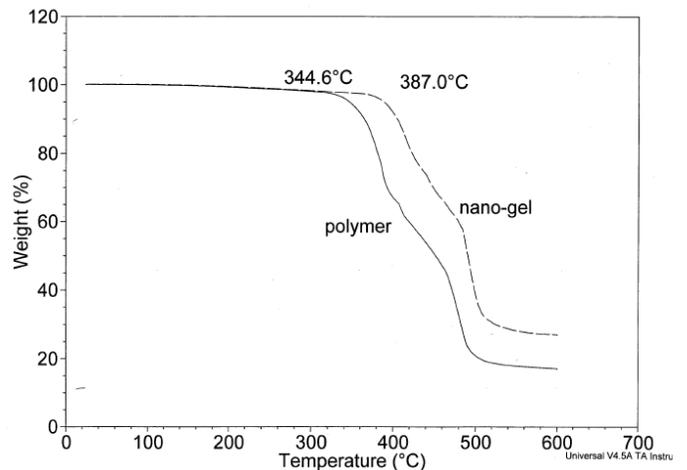
Figure 8: Thermogravimetric analysis for the polymer and nano-gel.

Figure 8 shows the Thermogravimetric analysis of the polymer and nano-gel at a heating rate 10°C/minute. Thermogravimetric analysis of the base polymer shows decomposition in the range of 344C. The nanogel under similar conditions decomposes around 386C with 5 % of the weight-loss taking place within the first 400C. Major decomposition of nano-gels moved to higher temperature. It appears that the nanoparticles act as a decomposition barrier to the polymer preventing them from decomposing and keeping the polymer stable in the nanogel.

Figure 9: SEM micrographs for the nano-gel at room temperature (A) low magnification, (B) High magnification. (C) SEM micrographs for the nano-gel heat-treated at100 ^{o}C for 4hrs.

The finer details of the particles and their distribution within polymer matrix were investigated using SEM. **Figure 9** shows the surface morphology of the nano-gel and heat-treated nano-gel at 100°C/4h. SEM clearly indicates individual or few agglomerated nanoparticles distributed within the polymer matrix. Nanoparticles (observed from SEM) wrapped by polymer in such a way that they maintain their individual identity even after heat-treatment at 100°C/4h. Nanoparticles slurry in absence of polymer sinters very easily at 100°C/4h (**Figure 3A**). SEM study suggests that the nanoparticles are well dispersed and thermally stable within the gel.
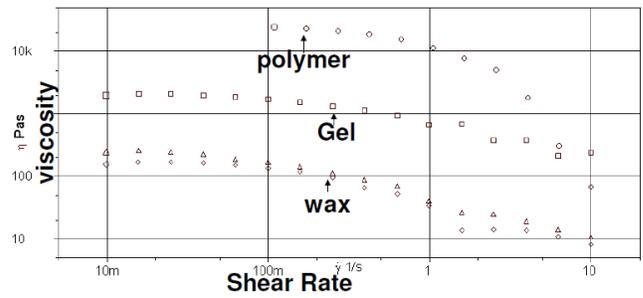
Figure 10: Viscosity of polymer, gel, liquid like materials as a function of frequency.

The Nano-gel showed lower viscosity compared to the base polymer. Viscosities of the base polymer and the nano-gels are in the range of 10,000 Pa s, and 1000 Pa s, respectively. Low flow liquid like materials showed viscosity in the range of 100-200 Pa s and the viscosity decreased to 0.5 Pa s (500cp) when oil based nanofluids were used. Viscosity is minimum for solvent based nanofluids (5-40 cp). **Figure 10** shows the viscosity of base polymer, gel, and liquid-like materials (wax) as a function of frequency.
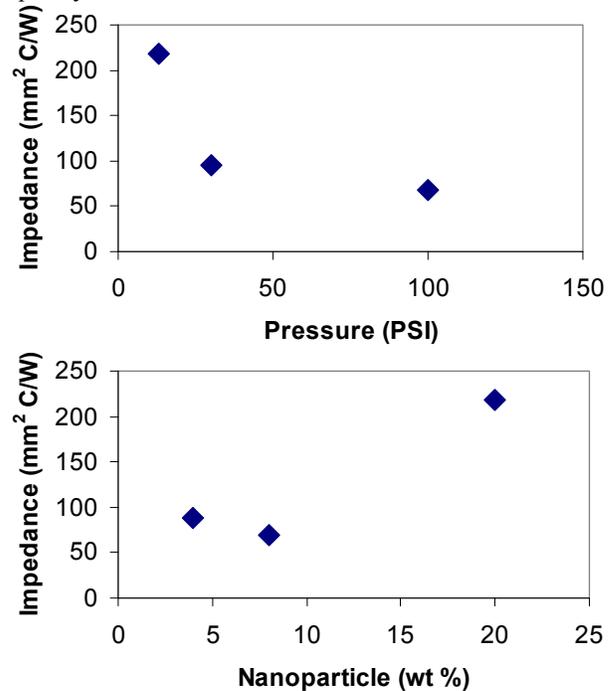
Figure 11: (A) Thermal impedance Vs Pressure and (B) Thermal impedance Vs concentration measured at 15 PSI.

Figure 11A shows the thermal impedance of 20% nano-gel as a function of pressure. Gel impedance decreased with pressure, around 65% and 75% impedance drop from 15 PSI to 30 PSI and 100 PSI, respectively. A sharp decrease in impedance is observed at 30 PSI, and thereafter it decreases slowly. Nano-gel thermal impedance increased with viscosity at room temperature (25 ^{o}C), around 10% and 30% impedance increase from 200 Pa s to 1000Pa s, respectively.

Interestingly the impedence of the nanogels remains unchanged after several days at room temperature. The thermal impedance was changed from 60 mm^2 C/W to 65 mm^2 C/W after 90 hrs at room temperature (25 ^{o}C). No change in impedance indicates that gels are stable for TIM applications. Stability of the nano-gel was further evaluated using high temperature heating. 5-10 nm nanoparticles sintered even at 100 ^{o}C (**Figure 3A**) and color changes from black to silver were observed. Here we have used nanogels heated at 100-125 ^{o}C for significant time (~4hrs) but did not show color changes. SEM study suggests (**Figure 9**) that there are no particle size or distribution changes after heat-treatment. The viscosity of liquid like material was 200-400 times more than nano-oils. Both systems are show similar impedance in the range of 55-65 mm^2 C/W at 30 PSI. This indicates that liquid like materials and oil form similar bondlines at 30 PSI for producing similar impedances.

4. Conclusions

A variety of micro-filled conducting adhesives modified with nano particles were evaluated for thermal interface material (TIM) applications. The addition of nanoparticles reduces the thermal impedance of micro-filled conducting adhesives. LMP based system diffuse at relatively lower temperature than nano-micro particles to produce lower thermal impedance. Nanogels with particles ranging from 5-10 nm and sintered nanopaste show similar impedances. Liquid-like materials and oil-based nanofluids generate thin bondlines for low impedance. LMP based or sintered pastes are the most suitable for obtaining low thermal impedance Z-joints. As the demand grows for tunable viscosities for TIM, nanomaterials will continue to provide unique opportunities. The strategy presented here may be extended to other nanomaterials suitable for TIM. Detailed characterizations of nanogels, nanofluids, nanopastes and corresponding thermal property evaluations are in progress.

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