Nanomaterials for "Green" Electronics

Rabindra N. Das , Konstantinos I. Papathomas, 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 examines the use of nanomaterials in the area of "green" technology. A variety of green materials for advanced organic packaging have been developed. These include capacitors and resistors as embedded passives, resin coated Cu (RCC) as buildup layers, highly conducting nano-micro media for Z-interconnects, lead free assembly paste, ZnO based additives, magnetic materials, inductors and thermal interface materials (TIM). Nanocomposites can provide high capacitance densities, ranging from 5 nf/inch^2 to 25 nF/inch^2, depending on composition, particle size and film thickness. The electrical properties of capacitors fabricated from $BaTiO_3$-epoxy nanocomposites showed a stable capacitance over a temperature range from 20°C to 120 °C. A variety of printable discrete resistors with different sheet resistances, ranging from 1 ohm to 120 Mohm, processed utilizing a large panel format (19.5 x 24 inches) have been fabricated. Low resistivity nanocomposites, with volume resistivity in the range of 10^{-4} ohm-cm to 10^{-6} ohm-cm depending on composition, particle size, and loading can be used as conductive joints for high frequency and high density interconnect applications. A variety of metals including Cu, Ag, LMP (low melting point) and LMP-coated Cu fillers have been used to make halogen free, lead free electrically conducting adhesive technology as an alternative to solders. Halogen free resin modified with ceramics/organic particles can produce low Dk resin coated Cu (RCC) with Dk value in the range between 4.2 and 2.5. Similarly, low loss RCC materials can be produced by combining HF resin with low loss fillers. The mechanical strength of the various RCC was characterized by a 90 degree peel test and measurement of tensile strength. RCC exhibited peel strength with Gould's JTC-treated Cu as high as 6 lbs/inch for halogen free RCC. These halogen free RCC materials exhibit coefficients of thermal expansion (CTE), ranging from 27 ppm/°C to 32ppm/°C. The paper also describes a nanoparticle dispersion approach to prepare nanogels and nanofluids as thermal interface materials. Altogether, this is a new direction in the development of Green Packages and more specifically in the development of coreless substrates for semiconductor packaging.

1. Introduction:

The electronics industry is under pressure from environmental groups to remove potentially toxic compounds such as brominated flame retardants, lead based solders and other environmental pollutants from consumer products and electronics **[1]**. It has been estimated that a 2g microchip requires 1.6 kg of secondary fossil fuels, 72 gm of chemicals, 32 kg of water, and 0.7 kg of elemental gases **[2]**. European Union (EU) generates ~ 8 million tons of electronic/electrical waste every year. In 2006, Americans scrapped around 400 million electronic items and generated around 2.9 million tons of e-waste **[3]**. Growing evidence shows that wastes are making their way into the environment. The chemicals may cause health problems, prompting many nations to ban or suspend their use in new consumer goods.

In recent years, significant progress has been achieved in the development of environmentally friendly semiconductor packaging technology using various green materials **[4]**. This trend is driven by demand for low cost, large area; lead free, halogen free and RoHS compliant devices. For these purposes, green organic and polymeric materials have been widely pursued since they offer numerous advantages for easy low temperature processing, compatibility with organic substrates, and great opportunities for structural modifications. Nanocomposites provide the greatest potential benefit for high density, high speed, miniaturized electronic packaging. The small dimensions, strength and the remarkable physical and electrical properties of these structures make them a very unique material with a whole range of promising applications. Several nanocomposites have been reported for advanced packaging applications. Although several nanocomposites are available for the advancement of semiconductor packaging technology, the authors believe that there is potential room for improvement of the existing materials, so that low processing temperature, environmentally friendly and cost effective processes / materials can be developed for large scale production. Nanocomposite should meet the following basic requirements in order to achieve "green" levels in an organic substrate/ materials **[5]**:

- Pb free (Limit: 1000ppm)
- Hg free (Limit: 1000ppm)
- Cd free (Limit: 1000ppm)
- Cr^{+6} free (Limit: 1000ppm)
- Polybrominated biphenyl (1000ppm)
- Polybrominated diphenyl ether (1000ppm)
- Bromine (900ppm)
- Chlorine (900ppm)
- Antimony trioxide (900 ppm)
- Antimony (750 ppm)
- TBTU : Tributyltin Oxide (not used)
- Red phosphours (not used)

In the present work we report novel "green" nanocomposites that have the potential to surpass conventional composites to produce materials, structures, manufacturing and circuit applications compatible with laminated organic substrates. Specifically, we discuss the electronic applications of green nanocomposites (**Figure 1**)

such as adhesives (both conductive and non-conductive), interlayer dielectrics (low Dk, low Df dielectrics), embedded passives (capacitors, resistors), circuits, etc. The use of halogen free (HF) epoxy and other chemistry based resins as the typical polymer matrix and a range of metal /ceramic fillers with particle size ranging from 10 nm to 10 microns is reported. The addition of different fillers into the polymer matrix controls the overall electrical properties of the composites. For example, adding zinc oxide nano particles into a polymer show laser like behavior upon optical pumping and addition of barium titanate ($BaTiO_3$) nanoparticles result in high capacitance. Halogen free materials have advantages in terms of manufacturability, processing temperatures, low moisture absorption, high glass transition temperatures, and versatility making it quite promising for advanced packaging. However, homogeneous dispersions of ceramic particles in the polymer matrix is a critical step in order to obtain films having uniform properties.

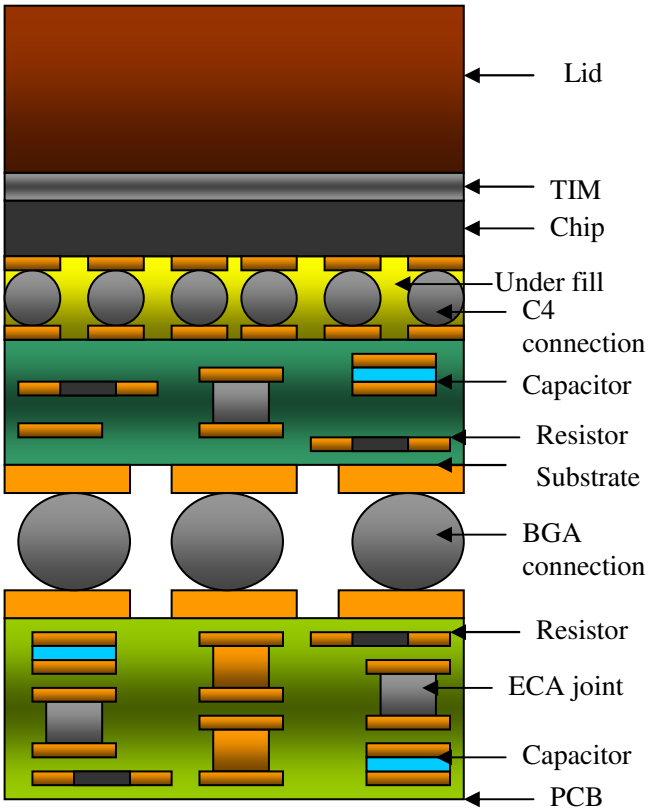

Figure 1: Overview of some of the potential applications of "green" nanomaterials in microelectronics.

2. Experimental Procedure

A variety of $BaTiO_3$, ZnO (zinc oxide), silver nano particles and their dispersion into halogen free polymer were investigated in order to achieve uniform prints and coatings. In a typical procedure, ZnO/Ag/$BaTiO_3$ halogen free polymer nanocomposites were prepared by mixing appropriate amounts of the nano powders and polymers in organic solvents. A thin film of this nanocomposite was then printed/coated on a copper substrate and cured. The content of metal/ceramic filler in the composites ranged from 40% to 95% by weight, depending on application. In the case of laminates, two thin films were prepared, dried, and then laminated together.

Electrical properties (capacitance, Dk, Df) of the nanocomposite thin films were measured at room temperature using an impedance/gain-phase analyzer (Model 4194A, HEWLETT-PACKARD). Surface morphology and particle distributions of nanocomposite films were characterized by a LEO 1550 scanning electron microscope (SEM). Resistance of materials was determined by Keithley micro-ohmmeter. Heat of reaction of HF materials was studied using a differential scanning calorimeter (DSC). Practical adhesion (90 degree peel test) and tensile strength were measured using an Instron (Model 1122) and MTS tensile tester, respectively.

3. Results and Discussion

In electronic applications, the HF materials are generally required to possess a wide range of favorable properties including high mechanical strength, good thermal stability and chemical resistance, low heat distortion, high resistance to aging, good electric insulation properties, consistent dimensional stability over a wide temperature range, good adhesion to glass and copper, high surface resistivity, low dielectric constant and loss factor, ease of drillability, low water absorption and high corrosion resistance.

In addition, a key requirement that is governed by the Underwriters' Laboratory (UL) is the ability to meet the flammability standard of UL 94-V0. In general thermosetting resins alone or in combinations with other additives, which are widely used in the electronic industry for PCB laminate applications, meet these requirements only because they contain approximately 20-40% brominated components. These brominated compounds have excellent flame-retardant properties. In the thermal processes, brominated compound can release corrosive byproducts such as HBr, Br_2 etc. The greatest concern of brominated compound is the risk of forming potential dioxins (extreme health hazards) by uncontrolled pyrolysis. We have developed halogen free laminating resins for substrate material. Halogen free resins have advantages for multilayer substrates in terms of processibility, thermal stability, low moisture absorption, high Tg, and versatility. However, processing and composition of HF materials is critical in order to achieve a high quality, reliable package. **Figure 2** shows typical examples of halogen free 2-4-2 package cross section where 4 layer internal core and subsequent 2 buildup layers (each side) used to form 2-4-2 structure. Halogen free resin coated copper (RCC) materials can be used to form buildup layers. The 4 layer internal core can have two resistance layers in the middle and the two capacitance layer sequentially applied on the surface. This allows multiple capacitance/resistance layers in a thin total structure. This paper examines the use of various halogen free polymer-ceramic nanocomposites in the area of substrates and assembly technology. Nevertheless, nanocomposites with desired properties, thickness, and tolerance present significant challenges.

3.1 Capacitors, resistors and inductors:

Embedded capacitors provide the greatest potential benefit for high density, high speed and low voltage IC packaging. Capacitors can be embedded into the interconnect substrate (printed wiring board, flex, MCM-L, interposer) to provide decoupling, bypass, termination, and frequency determining functions **[6]**. In order for embedded capacitors to be useful, the capacitive densities must be high enough to make layout areas reasonable. In this paper, we report novel $BaTiO_3$-HF Epoxy based polymer nanocomposites that have the potential to surpass conventional composite to produce high capacitance density, low loss, and applicable over large surface areas, thin film capacitors. Specifically, novel halogen free and lead free Resin Coated Copper Capacitive (RC3) nanocomposites capable of providing bulk decoupling capacitance for a conventional power-power core, or for a three layer Voltage-Ground-Voltage type power core, is described. The second capacitor in this case study was discrete capacitor. This capacitor is constructed using a screen/stencil process. In the case of laminates, two thin films were prepared, dried and then laminated together. RC3 with suitable thickness favors buildup layers for sequential buildup process as can be seen in **Figure 3**. On the other hand, laminates with proper processing can be used as a central core for buildups. It is interesting to note that the present process can manufacture large size (19.5 inch X 24 inch) halogen free RC3, laminates and printable capacitors.

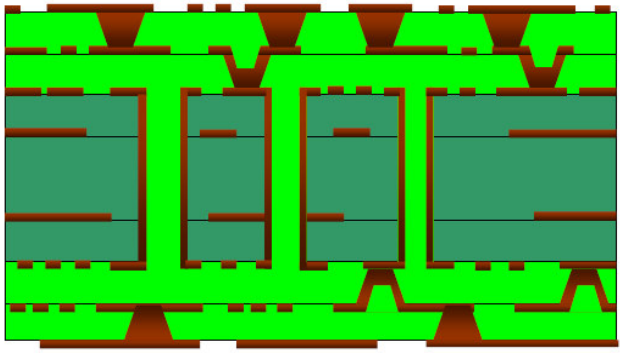

Figure 2: Halogen free substrate cross-section showing core and build-up layers.

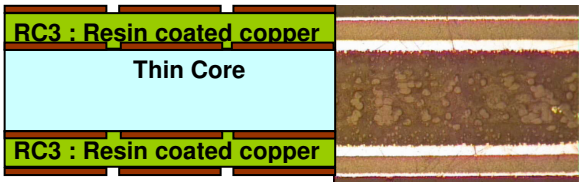

Figure 3: Schematic and Photograph of substrate build with ($BaTiO_3$)-HF polymer nanocomposite based RC3 materials.

In the nanocomposite, $BaTiO_3$ nano particles increase the overall dielectric constant, whereas the HF polymer matrix provides better processability and mechanical robustness. High temperature/pressure lamination was used to embed capacitors in multilayer printed circuit boards. The capacitor fabrication is based on a sequential build-up technology employing a first etched Cu electrode. After patterning of the electrode, the RC3 nanocomposite can be laminated within the PCB. **Figure 3** shows a schematic representation of RC3 based 4 layer core where embedded capacitors were fabricated from a regular thin RCC based substrate. A RC3 layer can reduce processing steps as well as package thickness. The fabricated embedded capacitor can also act as a sub-composite and can be laminated with other sub-composites for making a high layer count board with embedded capacitors.

The electrical properties of ~2-100 mm^2 capacitors fabricated from nanocomposite thin films showed high capacitance density ranging from 5 $nF/inch^2$ to 25 $nF/inch^2$, depending on composition, particle size and thickness of the coatings. Thin film capacitors fabricated from 40-60% v/v $BaTiO_3$ epoxy nanocomposites showed a capacitance density in the range of 5-20 $nF/inch^2$ that was stable over a frequency range of 1MHz to 10 MHz. Electrical properties of capacitors fabricated from ~70% v/v nanocomposite showed capacitance density of about 25 $nF/inch^2$. For the given composition, capacitance density and dielectric loss increase with decreasing thickness**. Figure 4A** shows the room temperature capacitance profile measured at 1.0 MHz - 5 MHz for a $BaTiO_3$-epoxy nanocomposite thin film as a typical representative example. It was found that with increasing frequency, the capacitance density decreased. Change in capacitance with frequency was less pronounced in the case of thicker films.

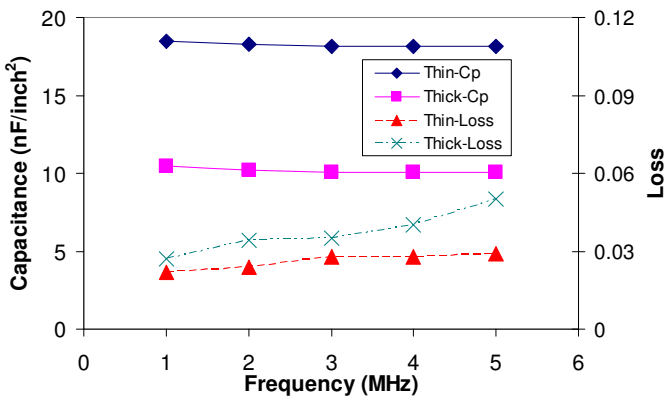

Figure 4A: Capacitance density and loss as a function of frequency and thickness (Thick-Cp and thick-loss represent capacitance density and loss of 10-15 microns film. Similarly, thin represent capacitance density and loss of 2-4 microns thin film.).

Most of the nanocomposites tested, 15µm through 35 µm thick, for which the $BaTiO_3$-based ceramic filler concentration was less than 50 vol%, passed 300 volt test. The outcome of high voltage testing depends upon the microstructure and thickness of the film. Nanocomposite film 15 to 25 microns thick and consisting of 1micron and 65 nm particles passed 300 volts, whereas 35 µm thick films passed 500 volt test. This is high enough for the nanocomposite to serve as an insulating material for embedded capacitors. Representative examples of temperature profiles (20°C - 120°C) of thin film embedded capacitors are shown in **Figure 4B.** We have used around 15 individual capacitors for high

temperature testing. The electrical properties of capacitors fabricated from halogen free nanocomposites showed a stable capacitance over a temperature range of 20°C to 120°C.

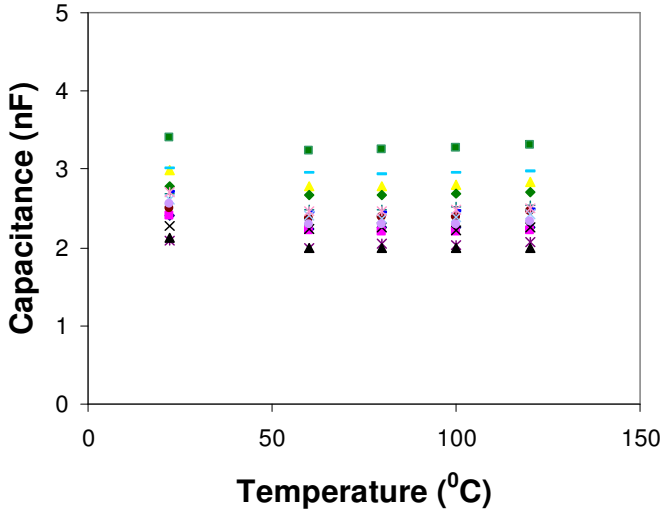

Figure 4B: Change in capacitance with temperature for ≥100 mm^2 embedded capacitors.

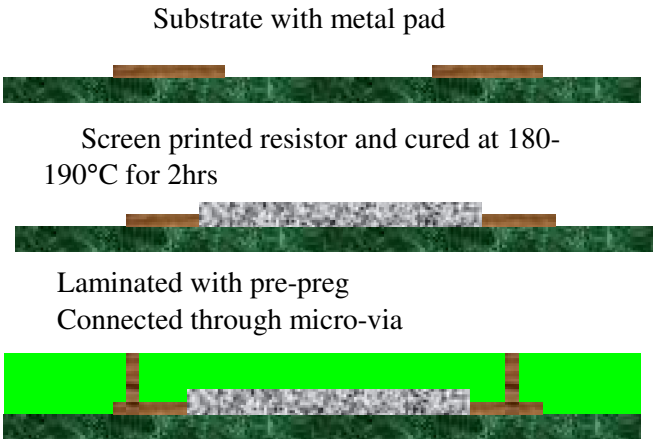

Figure 5A: Schematic presentation for making thin film embedded resistors.

A novel class of HF polymer nanocomposites is also attractive for resistor applications because variable resistor materials can be formed simply by changing the metal insulator ratio. These compositions, however, have practical advantage only when they are capable of being printed in the internal layers of circuit boards. **Figure 5A** shows a flow chart for making screen printed discrete embedded resistors. Resistance values are defined by the feature size, thickness and the polymer-ceramic compositions. We have developed various discrete resistors with sheet resistance ranging from 1 ohm to 120 Mohm. Resistors in various ranges offer low temperature processing and resistor materials can be printed in the same internal layer. Representative examples of temperature profiles (25°C -150°C) of thin film resistors are shown in **Figure 5B.** The electrical properties of resistors fabricated from HF nanocomposites showed a stable resistance over this temperature range.

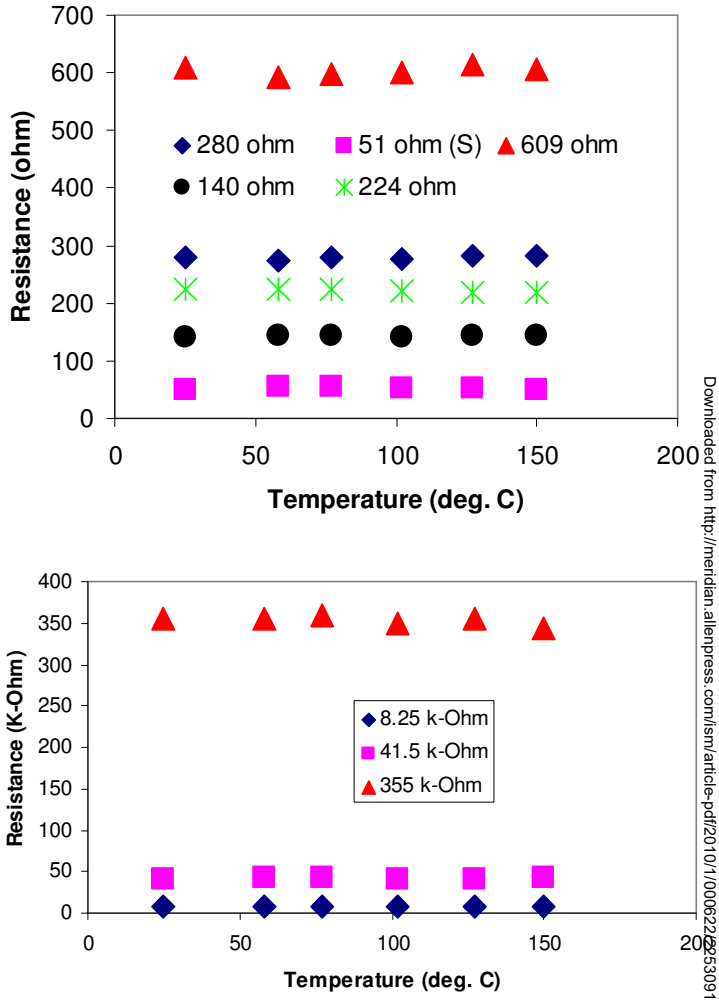

Figure 5B: Change in resistance with temperature for different resistors.

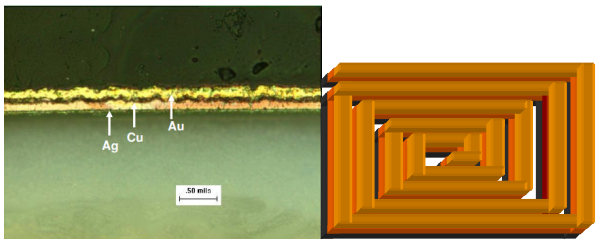

Figure 5C: Cross section (left) and schematic of multilayered spiral inductors

Ink-jet printing of spiral structures can be used to form inductors. The spacing in the spiral and the resistance will dictate quality of inductors. High resistance causes thermal loss and, therefore, is not suitable for inductors. Here we have deposited multi metal layers on ink-jet printed lines to increase current carrying capacity or conductance. High conductance spirals can generate higher magnetic field at the same voltage and thus can provide higher inductance in smaller packages. We have used a variety of multi metal layers including electroless Cu, immersion gold, electroless gold, electroless palladium, electroless nickel, etc. **Figure 5C**

shows a representative example of spiral inductors. Multi metal layer deposition on spirals reduces line resistance to hundreds of milliohms.

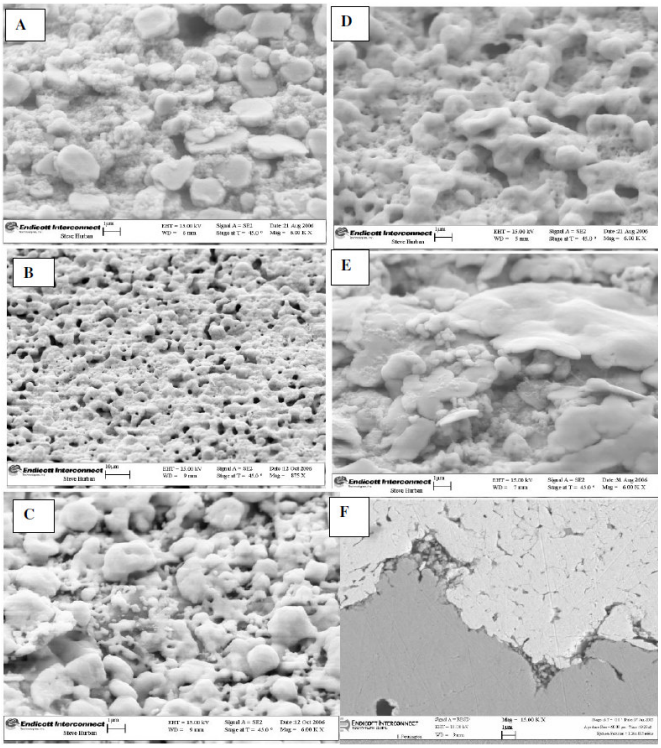

Figure 6: SEM micrographs for the nano-micro filled silver based conducting adhesives; (A) un-sintered at 200 ^{0}C, (B)-(D) sintered at (275 $\pm$10) ^{0}C, (E) un-sintered at 300 ^{0}C, and (F) sintered at 365 ^{0}C.

3.2 Conducting adhesives for interconnects:

Greater I/O density at the die level, coupled with more demanding performance requirements, is driving the need for improved wiring density and a concomitant reduction in feature sizes for electronic packages, and alternatives to the traditional plated through hole are required for high frequency and high density interconnect applications. One method of extending wiring density is a strategy that allows for metal-to-metal z-axis interconnection of subcomposites during lamination to form a composite structure **[7]**. There has been increasing interest in using electrically conductive adhesives as interconnecting materials in the electronics industry. Conductive adhesives are composites of polymer resin and conductive fillers. Metal–to-metal bonding between conductive fillers provides electrical conductivity, whereas a polymer resin provides better processability and mechanical robustness. Conductive adhesives have been used to fill vias in subcomposite structures, and form conductive joints to metal planes during lamination to adjoining circuitized cores. Typically, adhesives formulated using controlled-sized micro particles have been used to fill small diameter holes for Z-interconnect applications. In the present study, epoxy resin of micro-filled adhesives was replaced with halogen free resin to study electrical performance. Nano particles were mixed with micro-particles to improve sintering behavior of the adhesives. Halogen free polymer will maintain overall mechanical strength without compromising electrical conductivity. Adhesives exhibited volume resistivity ranging from 10^{-4} ohm-cm to 10^{-6} ohm-cm depending on composition, particle size, and loading of the adhesives. It was found that with increasing curing temperature, the volume resistivity decreased due to sintering of metal particles **[7]**. Nano particles and halogen free polymer based adhesives show 50-80% sheet resistance drop when cured at 275°C instead of 200°C. The observation suggests that the sintering mechanisms are not affected by HF resin systems.

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 nanocomposites has been carried out, and the results of such an investigation are presented here. **Figure 6** shows SEM images of the specimens collected from nanocomposites with different sintering temperature, from lower temperature (**Figure 6A**) to higher (**Figure 6F**). As can be seen, 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 6A**). 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 6B-D**). Conductivity measurements show that the resistance drops 30-50% from 200C to 265C. In contrast, the nanocomposites synthesized with a nano-micro mixture show a much different morphology as can be seen in **Figures 6E-F**. The nanoparticles are less (low concentartion). They are not following the same sintering mechanism as observed for the nanocomposite shown in **Figures 6B-D**. Instead, most of the particles maintain their identity, as if they didn't sinter with temperature. **Figure 6** shows nanocomposites sintered at lower temperature and higher temperature. The observation suggests that the sintering mechanisms are different for the nanocomposites synthesized in the two different mixtures. Based upon the morphologies observed above, we suggest a sintering mechanism for the nanocomposites at low temperature as follows.

In the high-concentration region, nanoparticles are highly reactive due to immediate particle to particle contact. Moreover, the diffusion (sintering) of nanoparticles should be lower than that of the corresponding bulk solid. With the increase of size, the particles need higher temperature for diffusion to make a uniform metallic network. However, in the low-concentration region, the polymer plays an important role. In this region, the amount of polymer is sufficient to prevent metallic diffusion/sintering.

3.3 Lead free assembly paste:

Tin-lead solder has been widely used as interconnection material in electronic packaging due to its low melting temperatures and good wetting behavior on several metal finish surfaces. Electrically conductive adhesives can be an alternative to lead based solders. A variety of metals

including Cu, Ag, LMP and LMP-coated Cu based bumping adhesives have been used to form electrical and structural interconnects between the chip and package. The adhesive was applied onto substrates by printing. The content of metal in the adhesives ranged from 75% to 90% by weight. **Figure 7** displays a schematic of lead free conductive adhesive materials comprising conducting filler particles dispersed in halogen free polymer matrix for die attachment. Specially, we are investigating low melting filler based conductive adhesives which can be fused to achieve metallurgical bonding between adjacent particles and between the particle and contact surface. It is necessary to selectively deposit adhesive on the substrate pad surface using screen or stencil printing, or by using a dip process to selectively transfer adhesive to the stud area of flip chip (die), or use both techniques together and interconnect the stud bump with the substrate pad using thermal curing of conducting adhesives. It is also possible to use insulating particle (TiO_2) filled halogen free epoxy resin as an under fill material.

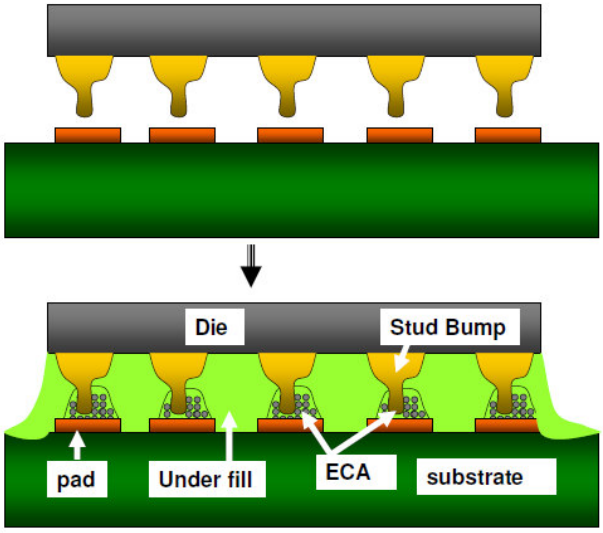

Figure 7: Schematic of die (flip chip) attachment with electrically conductive adhesives (ECA).

A combinatorial approach was applied to fabricate LMP-based, highly conductive assembly paste. **Figure 8A** shows an optical photograph of conductive adhesives with variable composition zones. Zones 1, 2, 3, and 4 have excess LMP that could melt and cause X-Y shorts during curing processes used in the fabrication of electronic circuitry. On the other hand, Zone 5 has excess metal. In a typical LMP system, the LMP metal melts and reduces interparticle resistance among the metallic particles. Less LMP was not sufficient to cover all the metal particles. Zone 6 (center part) shows minimum LMP content, but spread uniformly throughout the metallic network. This uniform mixture appears to be the best LMP-based conductive adhesive for Die attachments. Based on this experimental evidence, nano LMP-coated (~100 nm) particles were designed and synthesized. **Figure 8B** shows SEM micrographs of nano LMP-coated particles.

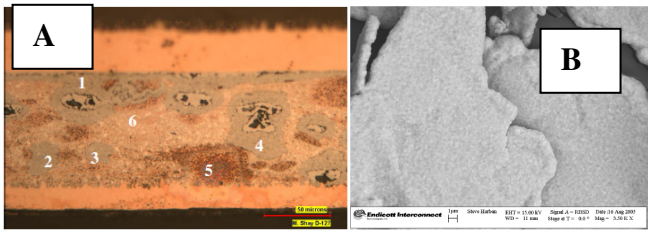

Figure 8: (A) Micrographs for the cross-sectional view of adhesives containing low melting point (LMP) fillers, silver and Cu particles, and (B)LMP coated Cu particle.

3.4 Halogen free (HF) resin coated copper (RCC) for buildups:

Low loss materials are important for high frequency and high speed applications. Low Dk materials are useful to reduce the dielectric thickness of the resulting circuit substrate. The rapidly growing wireless industry requires high performance materials to build low loss, high density, thermally stable integrated packages. The GHz operating frequency systems require substrate materials with lower loss (Df), low dielectric constant (Dk) and good power handling characteristics. Low loss is a critical requirement for lightweight portable devices for long battery life. Low Dk dielectrics not only lower line-to-line capacitance, but also reduce cross-talk problems between traces.

This paper describes ceramic filled low loss and low k materials compatible with laminated organic substrates. We introduced ceramic filled polymer systems where ceramic fillers and content dictate the property of composites. Pure silica and muti-component silica, boron nitride, alumina, zinc borate and several other low k and loss fillers were used as HF composites. The x, y, and z thermal expansion values for the various halogen free composites, both below and above the glass transition temperature, indicate that the coefficient of thermal expansion (CTE) is similar to the brominated RCC materials, ranging from of 27 o 32 ppm/°C. The lower CTE is due to the constraining properties of the fillers used to impart V0 rating. The above Tg CTE ranges between 76-95 ppm/°C. The glass transition temperatures were determined to be at 180 – 220°C as measured by the DSC middle point method, with the majority being in the range of 180°C. **Table 1** shows characteristic properties of silica filled halogen free materials. Bond strength of HF material laminates was evaluated using tensile strength measurements. Tensile strength was measured using an MTS tensile testing machine at a pulling rate of 0.025 inch per minute, and measuring until the joint ruptured. All HF laminates show high tensile strength (>6500 PSI) when laminated with Gould JTC-type Cu foils and did not show any failure. Here, adhesive (glue) used to attach laminates to test fixtures ruptured prior to the test structures. **Figure 9A** shows the room temperature Dk and loss profile measured in the frequency range of ~10 MHz to 1 GHz for an epoxy filled system as a typical representative example. Dielectric constant decreases with increasing frequency. As a case study, an example of halogen free RCC based multilayer construction for a flip-chip plastic ball grid array package is given. Two basic building blocks are used for this case study (**Figure 2**). One is a 4 layer internal core. The second

building block in this case study is the buildup layers. The 4 layer internal core is sandwiched between two layers of a HF materials-based dielectric. The signal (S) layers are comprised of copper features generated using a semi-additive (pattern plating) process. A line thickness of 12 µm was achieved with minimum dimensions for line width and space of 45 µm each. **Figure 9B** shows a silica filled buildup layer deposited on a core stricture.

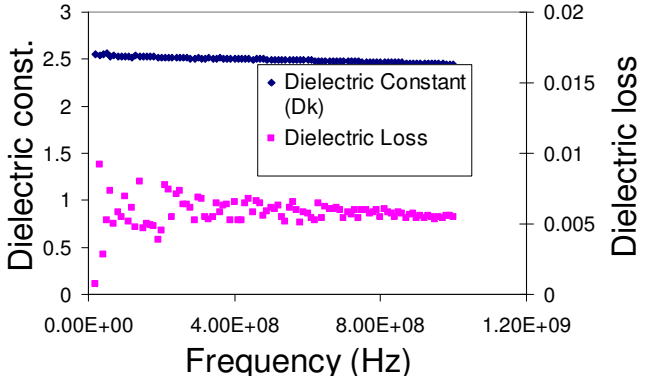

Figure 9A: Dielectric constant and loss as a function of frequency for epoxy based filled system.

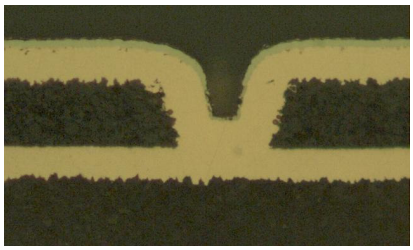

Figure 9B : Cross section of halogen free buildup layers on core materials.

3.5 Functional nanocomposites:

Functional nano-materials have received much attention because of their potential applications in optical, electronic and magnetic devices. Particular emphasis has been placed recently on nanostructured ZnO for optical devices in the blue to ultraviolet wavelength region because of its large direct bandgap of 3.4 eV. ZnO-based semiconductors can cover nearly the same wavelength range as GaN. The excitonic binding energy of ZnO is much larger than GaN-based compounds. A good deal of attention has been given to ZnO scattered systems which upon pumping exhibit a laser-like emission described by the term random laser **[8]**.

In parallel significant research work has been focused on magnetically active nanocomposites. Magnetic nanoparticles have excellent microwave absorption properties. These are widely used as electromagnetic absorbers in radiation shielding. Magnetically active nanocomposites can function as passive magnetic devices **[9]**. The nanocomposites are used to control inductance of the circuitry. A great deal of activity has been directed toward the development of printable magnetic nanocomposites. In a typical procedure different magnetic nanoparticles can be embedded into a HF epoxy matrix to provide passive magnetic devices such as inductors, antennas and transformers. **Figure 10** shows a variety of fine lines, spacing obtained from functional nanocomposites. It shows different line widths and spacing ranging from about 3 - 10 mils. Smaller features, such as ~2 mil dots, can also be printed. All these features can be used selectively to improve localized properties for multifunctional devices.

Table 1: Characteristic properties of silica filled halogen free materials

Average dielectric Constant (Dk) Measured frequency : 1-2.5 GHz	3.14
Dielectric loss at 1MHz	0.006
Tg of cured sample (DSC mid. point)	218 °C
T-260 with Cu	>120 minutes
Flammability, rating	V0
PCT, 60 minutes	8/8 pass
Moisture, 24 hr. RT - %	0.27
90 degree peel test with 0.5 oz Cu : lb/in	6.00
Thermal Expansion (x,y,z below Tg, ppm/C)	30.00
Thermal Expansion (x,y,z above Tg, ppm/C)	76
Tensile Strength	No fail, glue ruptured

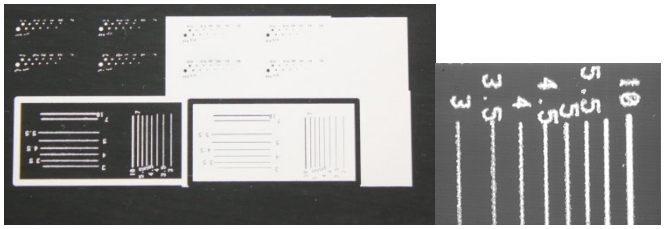

Figure 10: ZnO nanocomposite deposited on different surface. Picture reveals both layer as well as very selective depositions.

3.6 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. 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 [**10-11**]. In parallel significant research work has focused on nanopastes for Z-axis interconnections, 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.

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.

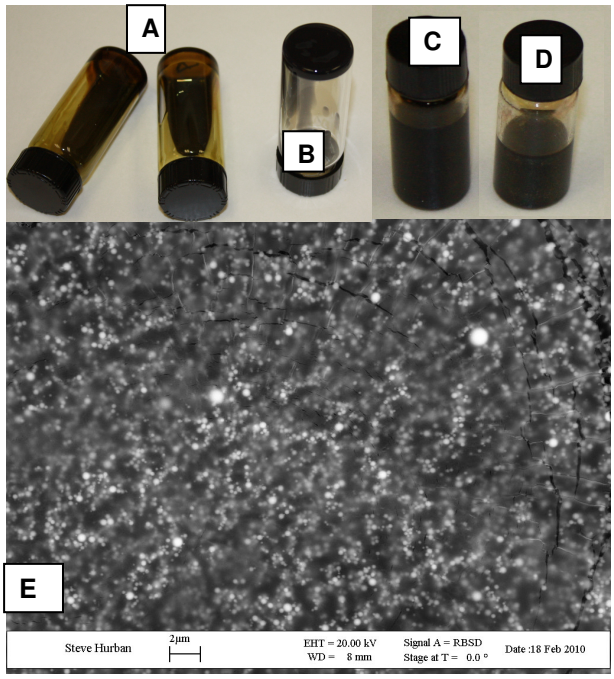

Figure 11: Photographs and flow characteristics of (A) Liquid like materials, (B) nano-Gel, (C) Oil based nanofluids, and (D) solvent based Nanofluids. (E) SEM micrographs for the nano-gel at room temperature.

Figure 11 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 11A-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. **Figure 11E** shows the surface morphology of the nano-gel. 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. SEM study suggests that the nanoparticles are well dispersed and thermally stable within the gel.

4. Conclusions:

"Green" nanocomposites can be used to enhance the conductivity of ECAs, form integrated resistors with controlled sheet resistance, and form capacitors with high capacitance density. The incorporation of silver nanoparticles and microparticles has been shown to improve the sintering behavior, and hence the conductivity, of the ECAs. A variety of green nanocomposites well suited to fabrication of sequential buildup technology has been developed. These materials enable fine-feature definition with excellent control of layer thickness. The nanocomposites can produce low loss, low k dielectrics as buildup layers. Experiments demonstrated that coating material is suitable for SBU whereas screen or contact printing is suitable for conducting lead free adhesives for interconnects, thermal interface materials (TIM) and die-attachments. Collectively, the results suggest that green materials may be attractive for a range of applications, not only where green technology is required, but also in large-area microelectronics to produce complex electronic packaging.

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