Abstract:

Printing technologies provide a simple solution to build electronic circuits on low cost flexible substrates. Nanocomposites will play an important role for developing advanced printable technology. Advanced printing is relatively new technology and needs more characterization and optimization for practical applications. In the present paper, we examine the use of nanocomposites or materials in the area of printing technology. A variety of printable nanomaterials for electronic packaging have been developed. This includes nano capacitors and resistors as embedded passives, nano magnetic materials, multifunctional materials, etc. Nanocomposites can provide high capacitance densities, ranging from 5nF/inch² to 25 nF/inch², depending on composition, particle size and film thickness. The electrical properties of capacitors fabricated from BaTiO₃-epoxy nanocomposites showed a stable capacitance and low loss over a temperature range from 25 °C to 100 °C. A variety of printable discrete resistors with different sheet resistances, ranging from 1 ohm to 120 Mohm, processed on large panels (19.5 inches x 24 inches) have been fabricated. Low resistivity nanocomposites, with volume resistivity in the range of 10⁻⁴ ohm-cm to 10⁶ ohm-cm depending on composition, particle size, and loading can be used as conductive joints for high frequency and high density interconnect applications. Thermosetting polymers modified with ceramics can produce low k dielectrics with k value in the range between 5.41 and 3.59. Similarly, low loss dielectric materials can be produced for mixing epoxy with silica or other low loss fillers. Nanocomposites can be very promising for electronic applications since they may potentially be fabricated entirely using similar printable polymer materials, so that low processing temperature, flexible and cost effective printable processes and materials can be developed for large scale production. An effort in this direction is presented in the paper.

Introduction:

In recent years significant progress has been achieved in the development of semiconductor packaging technology using various printing methods such as screen-printing, ink-jet printing, and microcontact printing. This trend is driven by demand for low cost, large area, flexible and lightweight devices. Since printing is inherently additive in nature, material and disposal costs are expected to be reduced, resulting in an extremely low net system cost. Most of the research activities in this printable area have been devoted to developing ink-jet solution-processable conductor materials [1-4]. Printable materials need to be chemically and physically inert to the other functional, dielectric, photoimageable materials processing in the same layer to preserve the structural and electrical integrity of devices/packages and they have to be operationally stable to sustain long operation life. For these purposes, organic and polymeric materials have been widely pursued since they offer numerous advantages including low temperature processing, compatibility with organic substrates, stable, and significant opportunity for structural modification. Nanocomposites provide the greatest potential benefit for high density, high speed, miniaturized advanced packaging. The small dimensions, strength and the remarkable physical and electrical properties of these structures make them very unique materials with a range of promising applications. Semiconductor devices based on nanocomposites are considered to be very promising for electronic applications since they may potentially be fabricated entirely using similar printable polymer technologies where different active fillers can be introduced within the same functional polymer system. Several nanocomposites have been reported for advanced packaging applications. Although several nanocomposites used for the advance of semiconductor packaging technology are not always printable, the authors believe that there is potential room for improvement of the existing materials, so that low processing temperature, flexible and cost effective printable processes and materials can be developed for large scale production. An effort in this direction is presented in the paper.

In this work we report novel printable 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 printable nanocomposites (Figure 1) such as conductive adhesives, interlayer dielectrics (low-k, low loss dielectrics), embedded passives (capacitors, resistors), circuits, etc. We are also investigating printable optically/magnetically active nanocomposite and polymeric materials for fabrication of devices such as inductors, embedded lasers, and optical interconnects. Here we have used epoxies as the typical polymer matrix and a range of metal/ceramic fillers with particle size ranging from 10 nm to 10 microns. Addition of different fillers into the epoxy matrix controls the overall electrical properties of the composites. For example, addition of zinc oxide nano particles into epoxy show laser like behavior upon optical pumping and addition of barium titanate (BaTiO₃) nanoparticle results in high capacitance. Thermosetting resins in general resins having advantages in terms of manufacturability, processing temperatures, low moisture absorption, high glass transition temperatures (Tg), and versatility make them quite promising for advanced packaging. However, homogeneous dispersions of ceramic particles in the epoxy matrix are a critical step in order to achieve uniform property films.
Figure 1: Overview of some of the potential applications of nanocomposites in microelectronics.

Figure 2: Various printing process (A) Screen Print with printed area (6 inchX12 inch), (B)-(F) enlarged screen print, (G)-(H) Ink-jet print, (I) micro contact Printing, and (J) Dispensing.

Experimental Procedure:
A variety of BaTiO₃, ZnO, silver nano particles and their dispersion into epoxy resin were investigated in order to achieve uniform prints. In a typical procedure, ZnO/Ag/BaTiO₃ epoxy nanocomposites were prepared by mixing appropriate amounts of the nano powders and epoxy resin in organic solvents. A thin film of this nanocomposite was then printed on a copper substrate and cured or laminated. The content of metal/ceramic filler in the composites ranged from 40% to 95% by weight, depending on application. The effects of polymers, surface modifications, particle size, and loading parameters are important for printing process. Particle sizes below 25 nm are used for ink-jet printing. Titania (~10 nm), silica (~10-20 nm), silver (~15-25 nm) nanoparticles in pure form or surface modified can be dispersed in water based solution. 80 nm or bigger particles were utilized in making pastes for screen printing. Dispersion of nanoparticles in the solution is necessary to formulate inks for ink-jet prints. For example, titania and zinc oxide dispersed well in acetic acid based solutions. Surface modified nanoparticles
typically dispersed well in organic solvents like NMP. In a typical surface modification procedure, BaTiO$_3$ powders (40 g) were mixed with a solution containing 2 g of N-phenylaminopropyltrimethoxysilane, ethanol (95 ml) and water (5 ml). The white suspension formed was ultrasonicated for 5 min then stirred at 70 °C for 1 h. The product was collected, washed with ethanol (120 ml x 2) and vacuum dried. Sometimes organically modified particles dispersed well in organic solvents. An Impedance Analyzer and a Keithley micro-ohmmeter were used for electrical characterization.

Results and Discussion:

Printable nanocomposites have potential applications at all levels of microelectronics (see Figure 1). This paper examines the use of nanocomposites in the area of printing technology. Printing processes have several advantages such as selective deposition, repair and re-print capability. However, printed features with desired properties, thickness and tolerance present significant challenges. In general, nanocomposite solutions are used for thin ink-jet printing and pastes are used for thick screen and contact printing. Nanocomposite concentration and corresponding viscosity is important for printing process. Ink-jet printing prefers low viscosity in the range of 7-10 cp. Low viscosity helps to generate submicron thin structure. Screen and contact printing prefer higher viscosity (100,000-150,000cp) thixotropes and generate 10-25 micron thick features. Conducting polymers / composites favor ink-jet printing for transistors but can use screen/contact printing for making lasers which is a surface phenomenon where surface particles upon optical pumping shows laser like behavior. Embedded resistors, capacitors, and conducting circuit lines can use ink-jet or screen printing for different features. Dielectric features are typically large and can use any of the known print techniques. Figure 2 shows various printings. Figure 2A-E represent screen printing process. It can be seen that screen print methods can produce line features in the range of 100 microns. Figure 2F-J represent ink-jet printings showing minimum line feature size in the range of 75-100 microns and ~50 microns dot patterned. Space between two ink-jet printed lines can be reduced to 50 microns. Figure 2K represents micro contact printing with minimum feature size around 100 microns. For the dispensing technique, feature sizes depend upon the materials viscosity and corresponding needle used to dispense materials. It can dispense different shapes with minimum around 20 mils (500 microns) dot (Figure 2L). In addition, we are developing flexible packages for variety of applications. Several classes of flexible materials can be used to form high-performance flexible packaging. We are investigating ink-jet printing for low cost flexible packages. Figure 2M represents ink-jet printing on flexible substrates.

Capacitors and resistors:

A novel class of polymer nanocomposites which has shown a high dielectric constant, is a BaTiO$_3$ epoxy nanocomposite. These are used to fabricate thin film embedded capacitors. 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 nanocomposite can be deposited and laminated within a printed wiring board (PCB). Nanocomposite can be directly deposited by printing. Figure 3 shows a flow chart for making screen printed discrete embedded capacitors and resistors. Capacitance values are defined by the feature size, thickness and dielectric constant of the polymer-ceramic compositions. Figure 4A shows a representative test vehicle (TV) and corresponding cross-sectional views of screen printed embedded capacitors and resistors. Measurement of electrical properties of capacitors fabricated from nanocomposite prints and having areas of ~2-100 mm$^2$ (smallest circle electrode 0.060 inch diameter and square was 0.109 inch x 0.109 inch) showed high capacitance density ranging from 5 nF/inch$^2$ to 25 nF/inch$^2$, depending on composition, particle size, and thickness of the prints. Thin film capacitors fabricated from 40-60% v/v BaTiO$_3$ epoxy nanocomposites showed a stable capacitance density in the range of 5-20 nF/inch$^2$ and low loss ~0.012-0.022. Measurement of electrical properties of capacitors fabricated from 70% v/v nanocomposite showed capacitance density of about 25 nF/inch$^2$. Capacitance density of BaTiO$_3$-epoxy polymer nanocomposites modified with nanomaterial was also investigated. Capacitance density of nanomaterials modified films were higher than BaTiO$_3$-epoxy nanocomposites.
Figure 3: Schematic presentation for making screen printable thin film embedded capacitors and resistors

Figure 4A: Representative test vehicle (TV) and corresponding cross-section view of screen printed embedded capacitors and resistors (Collaboration: Georgia Tech PRC and Nokia)

Figure 4B: Impedance profile of Capacitors
We have used Network Analyzer for high frequency measurements of printable embedded capacitors. The measurements were carried out from 45 MHz to 26 GHz. Figure 4B shows high frequency capacitance profile of 1 cm diameter capacitors. The curve fitting indicates that these capacitors are equivalent to 1.4 nF bulk capacitance. The excess inductance including probe, via and embedded capacitors was estimated to be 60 pH.

Figure 5: Printed resistors

Nanocomposites are 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. We have developed various discrete resistors with sheet resistance ranging from 1 ohm to 120 Mohm. Resistors in various ranges (e.g. 1 ohm, 5 ohms, 10 ohms, 50 ohms, 100 ohms etc.) can easily be made. Resistor materials can be printed in the same internal layer. Figure 5 shows printed resistors with different lines and spaces.

Inductors:

Ink-jet printing of spiral structures can be used to form inductors. The spacing in the spiral and resistance will dictate quality of inductors. High resistance causes thermal loss and therefore, is not suitable for inductors. Here we have deposited multi metal layer 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 6 shows representative example of multi-metal layer based inductors. Multi metal layer deposition reduces line resistance to hundreds of milliohms.

Figure 6: (A) Spiral inductors, and (B) cross section of multilayered spiral inductors

Conducting adhesives for interconnects:

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. Metal-to-metal bonding between conductive fillers provides electrical conductivity, whereas a polymer resin provides better processability and mechanical robustness. Nanocomposites can be printed or filled in a joining core to fabricate Z-axis interconnections in laminates. Conductive joints were formed during composite lamination using an electrically 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 interconnection among the circuitized subcomposites. Figure 7 shows a flow chart for making interconnects among the circuitized substrate.
ZnO based nanocomposites:
ZnO has been proposed as an interesting material 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. Much attention has been given to ZnO scattered systems that upon pumping exhibit laser-like emission described by the term random laser. A number of ZnO based random lasers including ZnO polycrystalline film, powders [5], ZnO microlasers [6], ZnO based hybrids[7,8] etc. have been developed. In conventional lasers, photons reflected back and forth through a cavity stimulate the emission of more photons thereby helping to build up an intense coherent radiation beam (Fig. 8A) [9]. A similar effect can be produced in a disordered medium containing semiconductor particles or in a finely ground semiconductor powder. If the particles or grains are close enough – less than the wavelength of light – the photons form closed loops. As a result the light is scattered passing through the same grains, just as in an ordinary laser, light bounces back and forth between the mirrors leading to light amplification. Wiersma [9] suggested several possible applications of ZnO based random lasers in to variety of new miniaturized optical devices. Das and Giannelis developed a variety of ZnO polymer nanocomposites. Epoxy, PDMS (polydimethylsiloxane) and PMMA (polymethylmethacrylate) based ZnO nanocomposites show lasing at around 385 nm (blue-violet region). When ZnO dispersed in a fluorescent polymer like poly[2-methoxy-5-(2’-ethylhexyloxy)-p-phenylene vinylene](MEH-PPV), it shows lasing at around 610 nm (red region). Furthermore, Zinc oxide is useful as piezoelectric and sensor materials. This material can be used as filler for capacitance layers where ZnO improves microstructure and film quality of barium titanate epoxy capacitors. Figure 8B shows variety of fine lines, spacing obtained from printable ZnO nanocomposites. It shows different line widths and spacings ranging from about 3.5 - 10 mils. Smaller features, such as ~2 mil dots, can also be printed. All these features can be used as random lasers or capacitance or optical shielding layer. Thus it is possible to use printable ZnO as multifunctional materials for devices.

Figure 7: Schematic presentation for making screen printable Interconnects

Figure 8A: Schematic of a conventional (left) and random laser (right) (Ref. 9). ZnO nanocomposites shows laser like behavior upon optical pumping.
Magnetically active nanocomposites:

Another attractive nanocomposite is magnetically active nanocomposites. Magnetic nanoparticles have excellent microwave absorption properties. These are widely used as electromagnetic absorbers in radiation shielding. Also, high density recording media uses these particles [10, 11]. These materials are also used in microwave based communication systems functioning at frequencies of the order of $10^9$ Hz due to their low crystalline anisotropy [12, 13]. Preparation of nanocrystalline ferrite materials have been described in our previous paper [14]. Magnetically active nanocomposites can function as passive magnetic devices. 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 an epoxy matrix to provide passive magnetic devices such as inductors, antennas and transformers. Figure 9A represents transparent magnetic films which can be ink-jet or screen printed on any substrate. The SEM micrograph (Figure 9B) of magnetic powders depicts the basic powder morphology, where smallest visible particle can be identified with the crystallite or their aggregates. The micrograph exhibits sharp distribution of the platelet ferrite particles with particle size less than 100 nm.

Optical Waveguides:

Waveguides are important for high speed applications. Several polymer and nanocomposites are reported to be useful as waveguides. Zhang et al. [15], reported silver nanoparticle and rhodamine B based planar polymer multi-model waveguides. Silver nanoparticle concentration enhances the optical properties (Fluorescence) of rhodamine doped PMMA planar waveguides. Saj et al.[16], described plasmon waveguides composed of silver nanoplates arranged in several geometries to find the one with the lowest attenuation. They have investigated light propagation of 500-nm wavelength along different chains of silver nanoplates of sub-wavelength length and width and wavelength-size height. Yeo et al.[17], developed a new polymer-silica hybrid thermo-optic switch with significantly reduced crosstalk. The top cladding and the core layers are composed of polymer, while the bottom cladding layer is made of silica. Among various techniques, UV curing, micro-molding and replication are successful process to fabricate polymer waveguides. This paper presents a printing strategy for fabricating
waveguide devices. One strategy is to use screen print and subsequent photo process. Screen print will provide thickness control and photo-processing provides channels. Figure 2 shows ~ 50 micron thick printed line. Desired thickness of Clad or core layer can be achieved by single or multiple printing passes. We have also used contact printing for making waveguide channels. Contact printing is important in controlling the channel edge profile. Figure 10 shows contact printed channels where channel edges are angled. This kind of angle will be useful for light coupling. Good quality waveguides with low loss (approximately 0.04dB/cm) at 850nm can be fabricated with ink-jet printing. The major challenge of deploying this technology is in the formulation of the optical polymer with suitable viscosity and adhesion properties.

Low K and Low Loss composites:

Low loss materials are important for high frequency and high speed applications. Low k 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 which are important in many of these applications. Low loss is a critical requirement for lightweight portable devices for long battery life. Low-k dielectrics not only lower line-to-line capacitance, but also reduce cross-talk problems between traces. Organic polymers such as divinyl siloxane benzocyclobutene (DVS-BCB), a silicon-based polymer with high organic content and poly(arylene)ethers (PAE) are some examples of low K materials. Fluoropolymers, fluorinated polyimides, polyimide-silica hybrid and bismaleimide-triazine in combination with epoxies have been used as low loss and low k dielectric materials. This paper describes filled printable 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 multi-component silica, boron nitride, alumina and several other low k and loss fillers were used as printable composites. Figure 11A show variation of loss with silica concentrations measured at 1MHz. Dielectric loss decreases with increasing filler content. There is a threshold observed above 25 V%. Figure11B shows variation of Dk with frequency for different fillers as a representative example. Table 1 shows Dk and Df of different composites. Alumina composites show Dk ~ 5.41, boron nitride and silica have similar trend. Zinc borate modified Alumina composites and silica modified boron nitride composite show low loss. Screen printing and dispensing techniques are generally used for printing dielectric materials.

![Figure 11A](image)

**Figure 11A:** Epoxy-silica based system (loss drops with increasing silica concentration). Dielectric loss measured at 1MHz.

Reliability:

Reliability of the nanocomposites was ascertained by IR-reflow, thermal cycling, pressure cooker test (PCT), and solder shock. Change in capacitance after 3X IR-reflow and after 1000 cycles of deep thermal cycling (DTC) between -55°C and 125°C was within 5%. Change in capacitance after IR reflow (assembly) pre-conditioning (3X, 245 °C) and thermal shock up to 1400 cycles (-55C-125 °C) for large, medium and small embedded capacitors were less than 5% (Figure 12). Most of the nanocomposites in the test vehicle were stable after IR-reflow, PCT, and solder shock. Change of conductivity of electrically conducting adhesives after 3X-IR reflow at 220 °C was less than 5%. Some of the low loss materials were also exposed to PCT (4 hrs) followed by a 15 seconds solder dip at 260 °C. PCT and solder shock sometimes cause delamination. In general, solder dip/shock pick up the PCT induced defects and cause delamination. Initial PCT - solder dip experiment didn’t show any delamination. Detailed reliability testing of nanocomposites is under investigation.
Figure 11B: Dielectric constant as a function of frequency for epoxy-ceramic based system.

<table>
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<tr>
<th>Sample</th>
<th>Dk @2GHz</th>
<th>Df@2GHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron Nitride (BN)</td>
<td>3.59</td>
<td>.011</td>
</tr>
<tr>
<td>Boron Nitride – Silica (46/54)</td>
<td>4.15</td>
<td>.0098</td>
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<tr>
<td>Boron nitride –Silica (22/78)</td>
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<td>Silica</td>
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<tr>
<td>Alumina</td>
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<tr>
<td>Alumina-Zinc borate</td>
<td>4.82</td>
<td>.0088</td>
</tr>
</tbody>
</table>

Table 1: Dielectric constant (Dk) and Loss (Df) of Epoxy –ceramic composites.

Figure 12: Change in capacitance after IR reflow (assembly) pre-conditioning (3X, 245°C) and thermal shock up to 1400 cycles (-55C-125C) for large, medium and small capacitors for embedded capacitors
Conclusions:

Printable nanocomposites are promising not only because it is versatile but also economical compared to other methods. A variety of nanocomposites suitable in printable processes for the fabrication of selective and localized embedded component in PWB/LCC has been developed. The materials and processes enable fine feature and controlled thickness layer deposition. The result is accomplished by using ink-jet, screen, contact and dispensing processes. Experiments demonstrated that ink-jet printing and subsequent metal layer deposition is suitable for inductors whereas screen or contact printing is suitable for conducting adhesives for interconnect applications. Capacitors, resistors, ZnO and magnetic materials can use either ink-jet or screen/contact print processes based on their requirements and viscosity of solutions. Capacitors fabricated through printing process showed high capacitance and low loss and are reliable after IR-Reflow and DTC. Nanocomposites can produce variable resistance ranging from 1 ohm to 120 Mohm. Low k and loss materials can also be fabricated from nanocomposites. Overall, printable nanocomposites will be useful to produce multi-functional complex electronic packaging. The results also suggest that printable nanocomposites may be attractive for Roll-To-Roll manufacturing of large-area microelectronics such as roll-up displays, e-papers, keyboards, radiofrequency structures, medical devices etc.

Reference:

4. Yiliang Wu, Yuning Li, Ping Liu, Sandra Gardner, and Beng S. Ong, “Studies of Gold Nanoparticles as Precursors to Printed Conductive Features for Thin-Film Transistors” Chem. Mater. 2006, 18, 4627-4632