High Capacitance, Large Area, Thin Film, Nanocomposite Based Embedded Capacitors

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Abstract

This paper discusses thin film technology based on barium titanate ($BaTiO_3$)-epoxy polymer nanocomposites. In particular, we highlight recent developments on high capacitance, large area, thin film passives, their integration in PWB substrates and the reliability of the embedded capacitors. A variety of nanocomposite thin films ranging from 2 microns to 25 microns thick were processed on PWB substrates by liquid coating or printing processes. SEM micrographs showed uniform particle distribution in the coatings. The electrical performance of composites was characterized by dielectric constant (Dk), capacitance and dissipation factor (loss) measurements. Nanocomposites resulted in high capacitance density (10-100 nF/inch^2) and low loss (0.02-0.04) at 1 MHz. The manufacturability of these films and their reliability has been tested using large area (13 inch X 18 inch or 19.5 inch X 24 inch) test vehicles. Reliability of the test vehicles was ascertained by IR-reflow, thermal cycling, PCT (Pressure Cooker Test) and solder shock. Capacitors were stable after PCT and solder shock. Capacitance change was less than 5% after IR reflow (assembly) preconditioning (3X, 245 ^{o}C) and 1400 cycles DTC (Deep Thermal Cycle).

Introduction

Passives account for a very large part of today's electronic assemblies. This is particularly true for digital products such as cellular phones, camcorders, computers and defense devices. Market pressures for new products with more features, smaller size and lower cost virtually demand smaller, compact, complex circuit boards. An obvious strategy is to reduce the number of surface mounted passives by embedding them in the substrate or printed wire boards. In addition, current interconnect technology to accommodate surface mounted passives impose certain limits on board design, which limit the overall circuit speed. Embedding passives is one way to save substrate real estate, conversion cost, reduce parasitic effects and improve performance [1].

Among the various passives, embedded capacitors deserve special attention as they provide the greatest potential benefit for high density, high speed and low voltage IC packaging. Capacitors can be embedded into the interconnect substrates (printed wiring board, flex, MCM-L, interposer) to provide decoupling, bypass, termination, and frequency determining functions [2, 3]. In order for embedded capacitors to be useful, the capacitive densities must be high enough to make layout areas reasonable. Available commercial polymer composite technology is not adequate for high capacitance density thin film embedded passives. Several polymer nanocomposite studies so far have been focused on processing of high capacitance density thin films within small substrates/wafers [4-7]. One of the important processing issues in thin film polymer nanocomposite based capacitors is to achieve high capacitance density on large coatings.

In this paper, we report novel $BaTiO_3$-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, we are focusing on new composite dielectric materials that can be integrated into boards, LCC (laminate chip carrier) or roll-to-roll manufacturing processes. In the present composite, $BaTiO_3$ nano particles increase overall dielectric constant, whereas the polymer matrix provides better processability and mechanical robustness. The effects of particle size, thickness and loading parameters on the observed electrical performance and the reliability of the embedded capacitors are presented.

Experimental Procedure

A variety of $BaTiO_3$ nano particles and their dispersion into epoxy resin were investigated in order to achieve a thin uniform film. In a typical procedure, $BaTiO_3$ epoxy nanocomposites were prepared by mixing appropriate amounts of the $BaTiO_3$ nano powders and epoxy resin in organic solvents. A thin film of this nanocomposite was then deposited on a copper substrate and cured. In the case of laminates, two thin films were prepared, dried and then laminated together.

Electrical properties (capacitance, Dk, loss) of the nanocomposite thin films were measured at room temperature using an impedance /gain-phase analyzer (Model 4194A, HEWLETT-PACKARD). The dielectric constant/capacitance as a function of temperature was determined using a precision LCZ meter (Model 4277A, HEWLETT-PACKARD) at 1MHz. Surface morphology and particle distributions of nanocomposite films were characterized by a LEO 1550 SEM (scanning electron micrograph). Thicknesses of films were determined by Optical microscope and SEM.

Results and Discussion

A real challenge in the development of large area thin film nanocomposites is the incompatibility that exists between the typically hydrophilic nanoparticles and hydrophobic polymer matrix, which leads to nanoparticle agglomeration. As a result inferior coatings with poor performance are obtained. We have identified proper surface treatment that results in excellent dispersability of the nanoparticles and good quality, monolithic coatings when materials are subsequently deposited onto a metallized substrate. Surface treatment of ceramics depends on its' processing routes. Ramesh et al [7] reported silane treatment of hydro thermally prepared $BaTiO_3$ nano particles. **Figure 1** shows series of large area thin and printed films. Thickness of the as deposited on Cu substrate and cured nanocomposite leads to a noticeable color change as can be seen in **Figure 1(A)** and **Figure 1(B)**. 2-3 micron films are almost transparent and show Cu-substrates color. Film transparency reduces with increasing thickness and eventually become $BaTiO_3$ nanocomposites color. Figure 1(C) represents screen printed capacitor arrays. It is interesting to note that present technology can manufacture large size (19.5 inch X 24 inch) printable and thin film capacitors (see **Figure 1D**)

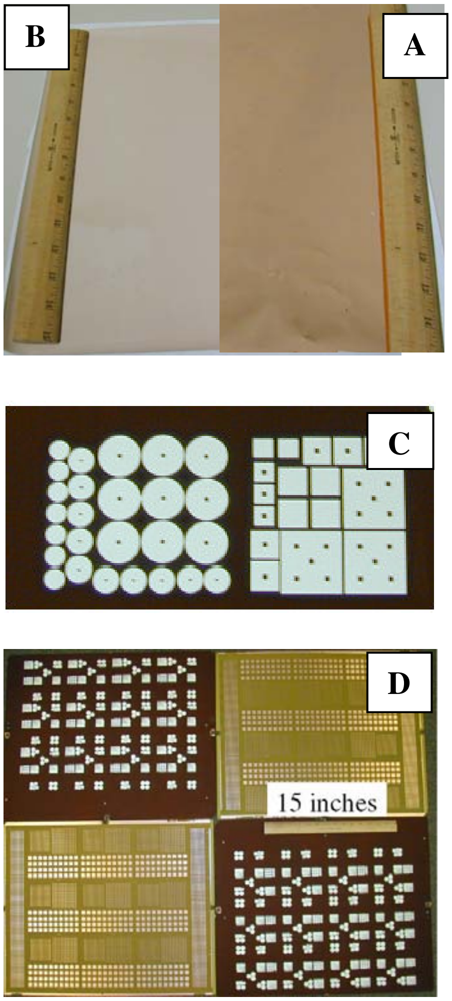

Figure 1: Photographs of ($BaTiO_3$)-epoxy polymer nanocomposite films (A) 2-3 microns films (B) 8-10 microns film (C) screen printed capacitors (1 inch X 1 inch array) (D) large size (19.5 inch X 24 inch) printable and thin film capacitors.

The finer details of the particles and their surface morphologies were investigated using SEM. **Figure 2** show the scanning electron micrographs of nanocomposite thin films. Nano particles formed uniform dispersion in the epoxy matrix. The particles in the epoxy matrix are so intimately compacted that analysis of individual particle is difficult. However, closer observation of the micrographs clearly reveals a uniform distribution of closely packed, well connected particles. Figure 2(A) and 2(B) show surface morphology of nanocomposites consist of 120 nm and 500 nm particles. Figure 2(C) shows surface morphology of nanocomposite prepared from 10 nm and 120 nm particles. Here small particles are well distributed throughout the thin film. 10 nm particles produce transparent films. Introduction of small particles improves overall transparency for use in photoimageable films for discrete capacitors.

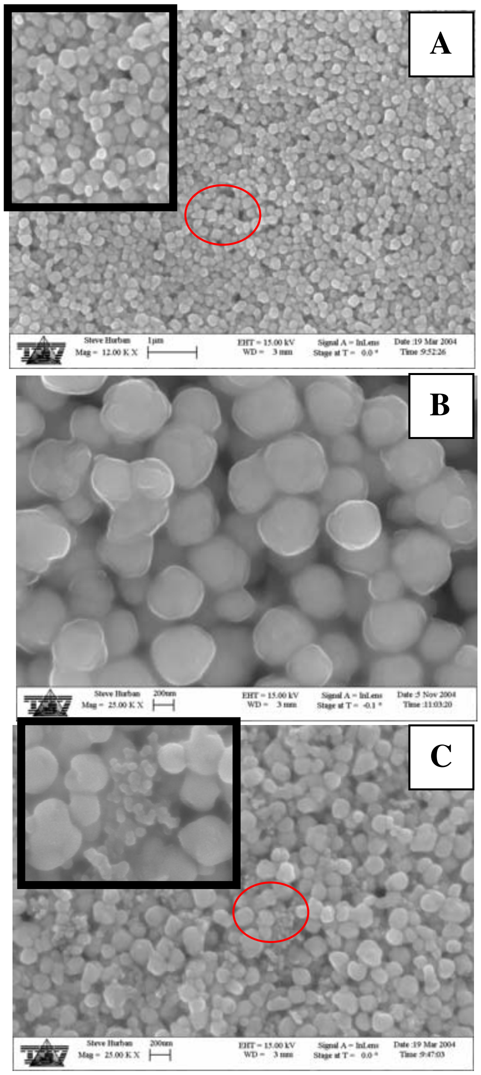

Figure2: Larger area SEM image of composite specimens: (A) 120 nm particles. Inset: displays larger magnification (B) 500 nm particles (C) 120 nm and 10 nm particles. Inset: displays larger magnification

Figure 3 shows cross sections of thin films sandwiched between two metal electrodes. It is possible to make a wide variety of films with different thickness. Desired thickness of the film can be achieved by controlling the viscosity of the coatings, composition and the number of layers deposited. In the present process, we can easily deposit thin films from about 2 microns to about 25 microns. **Figure 3** shows a variety of thin films with average thicknesses of 2 microns, 3 microns and 8.5 microns as typical representative examples. **Figure 4** shows cross sections of two thin films laminated with each other. Thicknesses of the films will contribute to the overall thickness of laminates. Thus, it is possible to prepare different thickness films and laminates using nanocomposites. Cross section SEM image of 2 microns film (**Figure 3A**) show well defined nanoparticles that help to maintain such a thin structure.

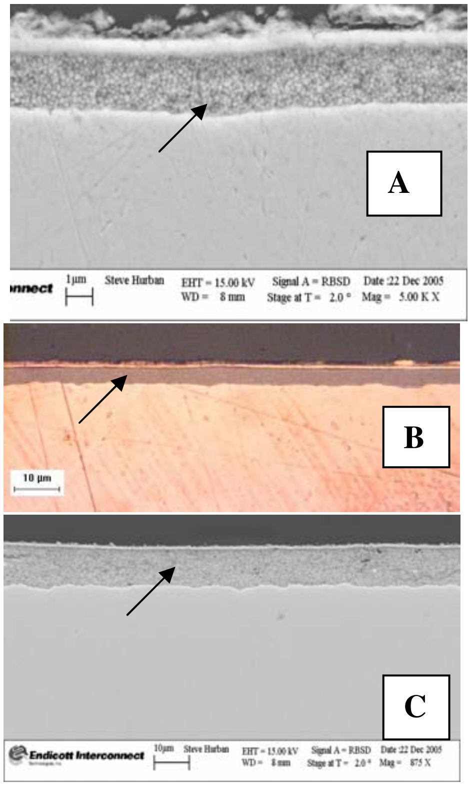

Figure 3: Cross sections of thin films (A) 2 micron, (B) 3 micron and (C) 8.5 microns**.**

The electrical properties of ~2-100 mm^2 capacitors fabricated from nanocomposite thin films showed high capacitance density ranging from 10 nF/inch^2 to 100 nF/inch^2, depending on composition, particle size and thickness of the coatings. **Figure 5** shows the dielectric constant (Dk) and dissipation factor variation of nanocomposites with varying filler content. Dk as well as loss increases with increasing filler content. Minimum Dk (3.7) and loss (0.017) was observed for pure epoxy. Thin film capacitors fabricated from 40-60% v/v $BaTiO_3$ epoxy nanocomposites showed a stable capacitance density in the range of 40-80nF/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 100nF/Inch^2. For a particular composition, capacitance density, as well as dielectric loss, increases with decreasing thickness**. Figure 6** shows the room temperature capacitance profile measured at 1MHz - 10 MHz for a $BaTiO_3$ epoxy nanocomposite thin film as a typical representative example. It was found that with increasing frequency (1-10 MHz), the capacitance density decreased. Change in capacitance with frequency was less pronounced in the case of thicker films. The breakdown voltage of all nanocomposites below 60 vol% was higher than $3x10^7$V/m, which is high enough for the nanocomposite to serve as an insulating material embedded capacitor. Similarly, tensile strength with 1 oz copper for all nanocomposites below 60 vol% was found to be higher than 3700 PSI.

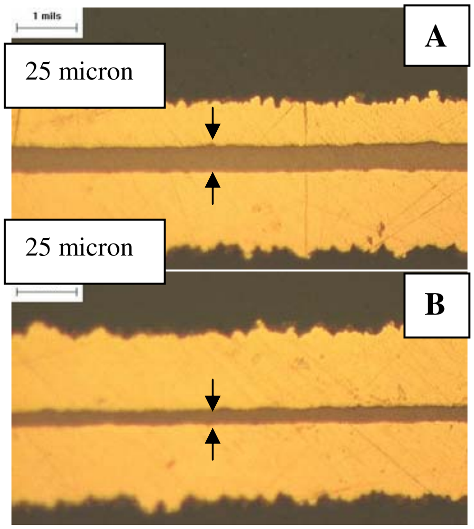

Figure 4: Cross sections of thin films laminated with each other (A) 10 micron laminates and (B) 5 micron laminates.

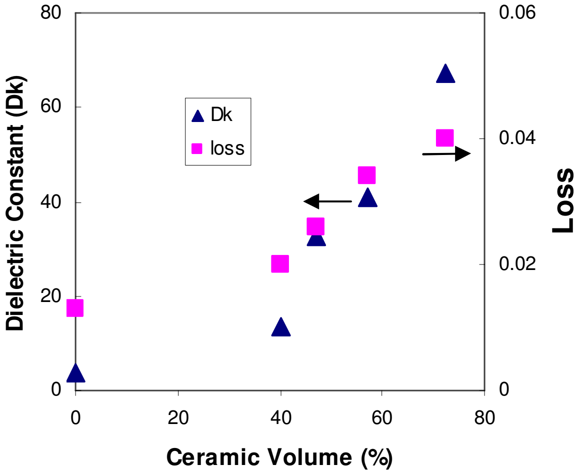

Figure 5: Dielectric constant (Dk) and dielectric loss versus loading

A variety of $BaTiO_3$ nanoparticles were used to prepare nanocomposites. For example, we have used hydrothermally processed 65 nm and 120 nm particles, as well as sol-gel processed 500 nm $BaTiO_3$ particles. All nanocomposite capacitors fabricated from $BaTiO_3$ with average particle size below 700 nm show stable high capacitance. It is difficult to establish a direct correlation between particle size and capacitance density in this work because the different sized $BaTiO_3$ nanoparticles were derived through different ceramic processing routes, resulting in different dielectric property/capacitance [8,9]. However, we could establish that at low filler content, finer particle composites show significantly higher capacitance density. **Figure 7** represents electrical properties of capacitors fabricated from different sized nanoparticle composites containing same $BaTiO_3$ to polymer ratio. Finer particles with higher surface area may have better particle to particle contact for improving overall property.

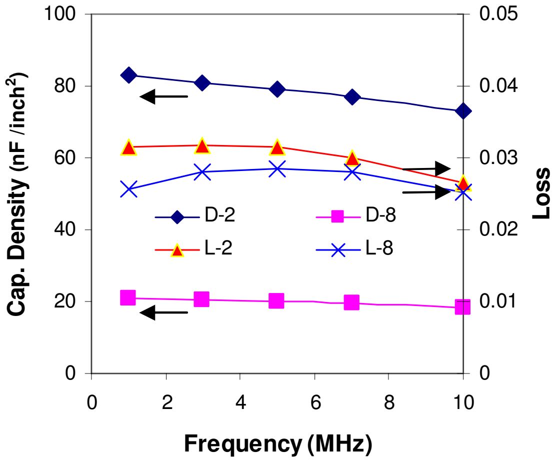

Figure 6: Capacitance density and loss as a function of frequency and thickness (D-8 and L-8 represent capacitance density and loss of 8.5 microns thin film. Similarly, D-2 and L-2 represent capacitance density and loss of 2 microns thin film.)

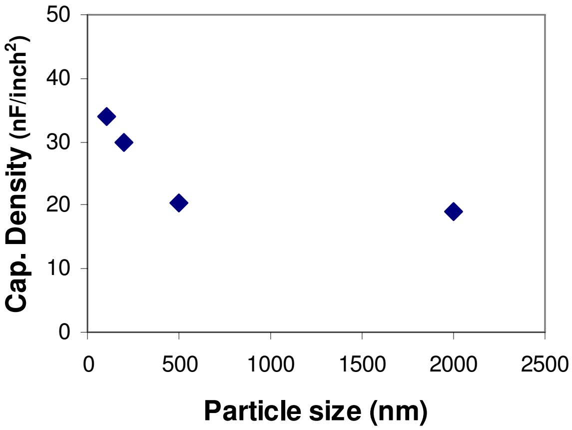

Figure 7: Capacitance change with particle size

$BaTiO_3$ epoxy nanocomposites were 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 PCB. Nanocomposite can be directly deposited either by liquid coating or screen printing. Alternatively, BaTiO3 epoxy nanocomposite thin films can be laminated and capacitor laminate can be used as the base substrate for subsequent build-up processing. **Figure 8** shows a general flow chart to make embedded capacitors fabricated from a capacitor base substrate. The fabricated embedded capacitor (shown in **Figure 9**) can also act as a sub-composite and can be laminated with other sub-composites for making high layer count board with Embedded capacitors. **Figure 10** shows a flow chart for making screen printed discrete embedded capacitors. In both cases, capacitance values are defined by the feature size, thickness and dielectric constant of the polymer-ceramic compositions. **Figure 11** shows a cross section of screen printed embedded capacitors.

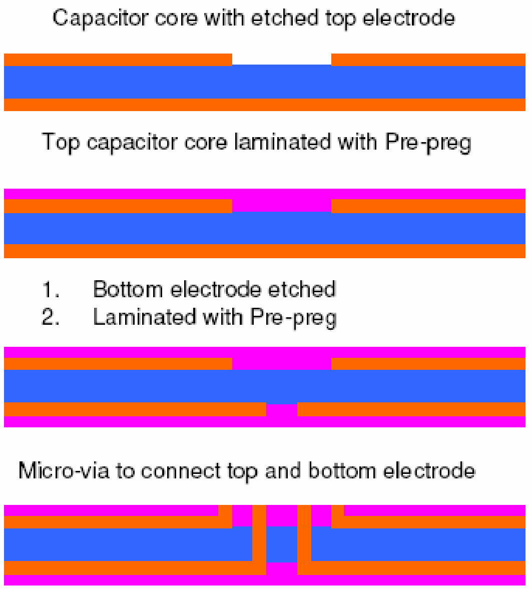

Figure 8: Schematic presentation for making thin film embedded capacitors.

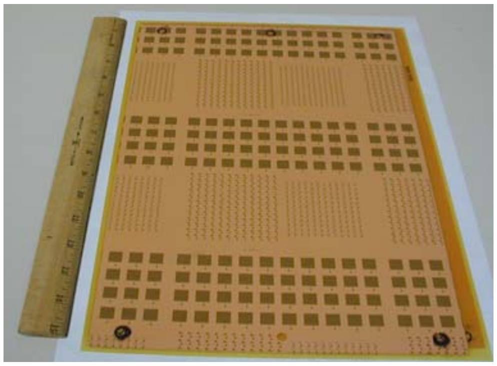

Figure 9: Thin film embedded capacitors

Reliability

Although embedded passives are more reliable by eliminating solder joints, they also introduce other potential defects such as cracks, material mismatch, delamination, etc. Embedded capacitors are of little value unless they can survive the same rigors of testing that modules or boards would receive. Reliability of the composites was ascertained by PCT, solder shock, IR-reflow and thermal cycling. **Table-1** summarizes reliability results.

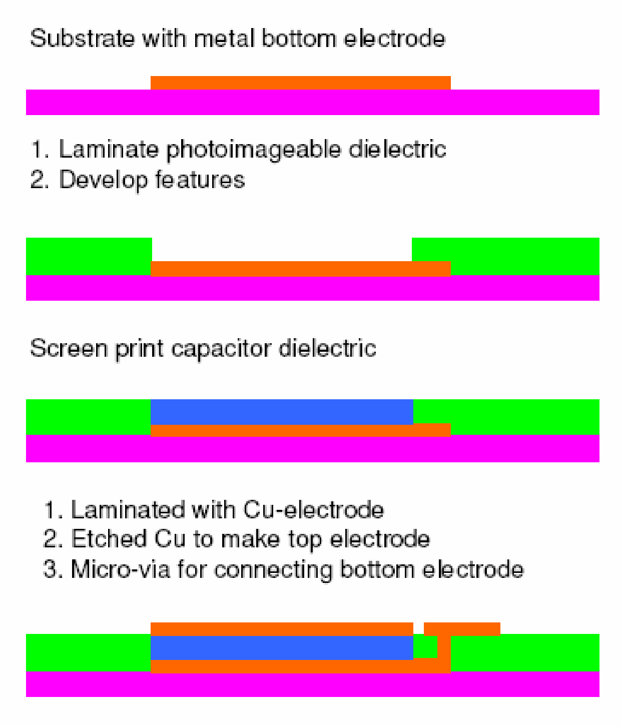

Figure 10: Schematic presentation for making screen printable thin film embedded capacitors

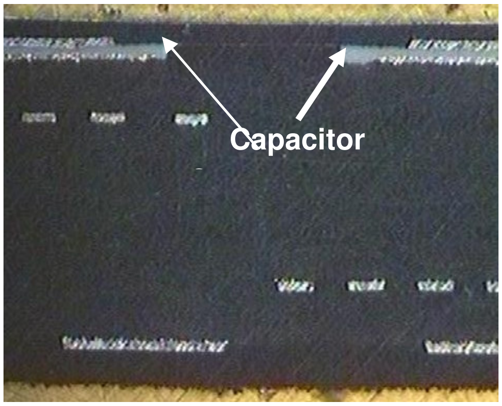

Figure 11: Cross section of embedded capacitors

Representative examples of temperature profiles (25 °C -100 °C) of thin film embedded capacitors are shown in **Figure 12.** The electrical properties of capacitors fabricated from $BaTiO_3$-epoxy nanocomposites showed a stable capacitance and low loss over a temperature range of 25 °C to 100 °C. The capacitance change was less than 10%. The loss tangent decreases with increasing temperature. Loss change is relatively large and is likely attributed to the base $BaTiO_3$ which typically show lower loss at higher temperatures. The loss begins to increase near the $BaTiO_3$ transition temperature [10,11]. Nanocomposites showed a 5-10 % increase in capacitance after PCT, where samples were exposed to 100 % humidity with a constant pressure 19 PSI at 121 °C. Even though capacitance density is relatively high after this test from original value, the effects are reversible with simple drying. This indicates that the effect is a water absorption phenomena rather than a defect-driven mechanism. Capacitors were also exposed to PCT (4hrs) followed by 15 seconds solder dip at 260 °C. There was no delamination observed after PCT and solder shock. In general, solder dip/shock will accentuate PCT induced defects and cause delamination. This also indicates that the change in capacitance after PCT was merely water absorption phenomenon and not a defect driven mechanism.

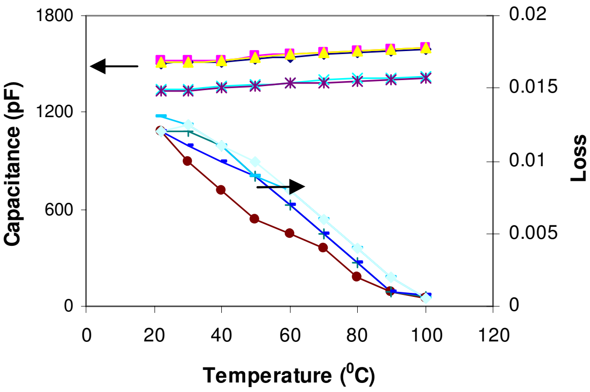

Figure 12: Change in capacitance and loss with Temperature for embedded capacitors

Capacitors, in some cases, have experienced larger changes (up to ~10%) after 1000 DTC (-55 °C to 125 °C, 10 minute soak) cycles. The initial 200-300 cycles showed the biggest change, while change was minimal after 300 cycles. This large capacitance change could be due to the lack of copper annealing of unassembled boards. We were able to overcome this large initial change by baking and / or IR reflow prior to thermal cycling. **Table 1** shows the capacitance change for the board used for IR reflow (assembly) preconditioning (3X, 245 °C) before thermal cycle. The reflowed board showed 3-4% capacitance reduction. All capacitors experienced less than 5% change after 3X, IR reflow and 1400 cycles of thermal cycle. Similar results (<5%) were observed after 1000 cycles DTC for baked samples (baking at 140 °C /4hrs). Change in capacitance with baking and /or IR reflow indicates copper annealing that could possibly stabilize capacitors prior to thermal cycling.

Conclusions

A thin film technology based on barium titanate ($BaTiO_3$)-epoxy polymer nanocomposites was developed to manufacture high performance embedded capacitors. The technology is able to produce high capacitance density (10 to 100 nF/inch^2), large area, thin film capacitors with controlled thickness from about 2 micron to about 25 microns for a series of $BaTiO_3$ epoxy nanocomposites. SEM micrographs showed uniform particle distribution in the composites. High temperature/pressure lamination was used to fabricate embedded test capacitors in a multilayer printed circuit board. Embedded test capacitors were stable with temperature profile (25-100 °C), PCT and solder shock. All capacitors experienced less than 5 % reduction after 3x IR reflow and 1400 cycles DTC.

Test	Property	Results
PCT (4hrs) at 121 °C with 100% humidity	Capacitance	5-10 % increase
Solder shock (15 seconds dip at 260 °C)	Bonding	Passed
PCT +Solder shock	Bonding	Passed
IR-reflow (245 °C, 3X)	Capacitance	<5%
Thermal Cycle (-55 to 125 °C)	Capacitance	~10 %
Bake(150 °C /4hrs) +1000 Thermal Cycle (-55 to 125 °C)	Capacitance	<5%
IR-reflow + 1400 thermal cycle	Capacitance	<5%

Table 1: Environmental test results

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