Improvements and Recent Advances in Nanocomposite Capacitors Using a Colloidal Technique

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Abstract

In this work, a colloidal technique is used to improve the dielectric properties of nanocomposite materials and to achieve thin film deposition (< 5 μm) on large area substrates using meniscus coating. Using this technique, improved particle dispersion is achieved, which in turn allows for higher volume loading (increased dielectric constant), small variation of dielectric constant across the substrate, and thin-film deposition with lower particle-induced defects. Appropriate dispersants and fillers particularly applicable to meniscus coating of these composite materials were found which allowed the coated and cured composite material to attain high relative dielectric constant (typical 40). Non-meniscus-coated samples with dielectric constants as high as 74 were achieved by varying the particle size distribution.

Key Words: colloidal, embedded, integrated, nanocomposite, capacitor, thin-film, large-area substrate, meniscus coating

1. Introduction:

Electronic packages are required to deliver higher and higher performance along with reduced size and weight, improved reliability, and reduced overall cost. To maintain this trend, integration of passives (resistors, capacitors and inductors) within the MCM dielectric layer beneath the integrated circuits (ICs) is required. Such multichip modules incorporating integrated passives are being studied at the Georgia Tech Packaging Research Center (PRC) to face this challenge. Among the various passive elements, capacitors are required in large number and occupy a large amount of space on a mixed-signal board. Thus, it is critical to integrate capacitors within the package to achieve high packaging efficiencies are to be achieved.

Dielectric materials used in thin-film capacitors are required to have a high dielectric constant, low dissipation factor, high thermal stability and good dielectric properties over a large bandwidth. Further, the integration of capacitors within the MCM layers are required to be low cost, should be relatively easy to fabricate on large area substrates, and should have minimum defects (e.g., pin-holes). There has been much work done toward realizing integrated capacitors in MCM-C and MCM-D based technologies along these lines [1]. However, less work has been reported with respect to integrating capacitors in MCM-L-based technologies. The biggest constraints of MCM-L-based technologies is the low processing temperature required of subsequent layers on base substrates and the thermo-mechanical properties of the base substrate effecting thin-film deposition. The Georgia Tech Packaging Research Center (PRC) has developed techniques for the integration of capacitors in MCM-L based technology [2, 3]. This has been carried out by combining appropriate attributes of thick-film polymer-ceramic composites technology and thin film processing technology, to produce patternable thin filled polymer layers referred to as *nanocomposites*. Specific capacitance as high as 22 nF/cm^2 has been reported, with relative dielectric constant of 65 and loss-tangent below 0.05 [2]. The goal of this work is to achieve higher specific capacitance (higher dielectric constant and/or lower film thickness) while maintaining good electrical and mechanical integrity of the dielectric films. In addition, the capacitors should be able to be fabricated on large area, low cost substrates using processes typical for the fabrication of interlayer dielectrics.

Techniques to further improve the electrical properties of polymer-ceramic composites can be understood from theoretical predictions [4], which indicate that the effective dielectric constant of the existing polymer-ceramic composites can be maximized by: (i) Higher filler loading (with a high dielectric constant ceramic); (ii) improvement in morphology (packing, size, and shape distribution); and (iii) high dielectric constant polymers and ceramics. With the given limited number of ceramic and polymer materials, options (i) and (ii) need to be exercised to improve the dielectric properties of nanocomposites. While our previous work focused on mixing and spin coating techniques [2,3], typical composites fabrication techniques, especially for non-thin-film applications, also include melt-blending [5-7]. The melt blend is formed and the mixture is then molded or cast to produce bulk films that are greater than 100 microns in thickness. In another approach, some investigators have tried to use mechanical pressing to fabricate the composite films [8]. Both of these techniques are difficult to extend into the thin film range. *In-situ* crystallization of barium titanate ceramic particles in a polymer matrix has also been investigated [9] using the hydrothermal technique [10]. However, the reported dielectric constants were low (< 20) perhaps due to the lack of a continuous network of ceramic particles.

To overcome the above-mentioned problems, in this study, a colloidal sol-gel processing concept is used to improve the dielectric properties of nanocomposites. The colloidal technique generally involves preparing a stable suspension of fine particles in a solvent (commonly referred to as a sol), coating a substrate to from a green film, and firing

the green film at elevated temperatures to form a dense ceramic film. Different variations of this technique such as tape-casting and slip-casting have been used to produce green ceramic bodies for various applications. In this study, the concept of colloidal processing is further extended to prepare polymer-ceramic composites. In addition to providing a better dispersion of particles (to prevent agglomeration), this technique also uses low viscosity sols which facilitates thin film processing. Systematic studies are performed with different types of polymer materials (including epoxies) and ceramic fillers to gain insight into the influence of degree of dispersion and microstructure on the electrical properties. In addition to material performance parameters, the ability to deposit thin films of these materials on large area substrates is also being studied as a processing issue.

2. Experimental

2.1. Material Selection:

Ceramic: The two types of filler particles used in this study were barium titanate (BT) powders (Cabot Performance Materials, average particle size 0.2 μm and TPL Inc., particle size 20 - 30 nm) and lead magnesium niobate-lead titanate (PMN-PT) powders (TAM ceramics, average particle size 0.05 -1 μm).
Polymers: Novalac-epoxy resin (SU-8, Shell Corpoation), benzocyclobutene (Dow Chemical), and polyimide (Dupont) were selected for their low molecular weight, photodefinition, and good electrical and mechanical properties.

2.2. Preparation of colloidal suspensions

The stability of colloidal sols is critical to obtain a uniform film with good packing density of filler particles [11]. Hence, the stability of colloidal sols was studied for each type of powder as a function of different variables including the volume fraction of filler, the type and amount of dispersant, and the type of solvent. The dispersants investigated include oleic acid (Fisher Scientific), polyacrylic acid (Fisher Scientific), Darvan 811 (R.T. Vanderbilt Company), and phosphate esters PS21A and PS230 (Witco Chemical Company). The solvents investigated were methyl ethyl ketone (MEK), propylene glycol methyl ether acetate, (PGMEA), mesitylene, and γ-butyrolactone (GBL). A number of different systems of dispersants, solvents, fillers, and polymers were studied and optimized to obtain stable suspensions, i.e., suspensions that did not show any appreciable settling of particles over a period of at least a few hours. The general procedure consisted of first dispersing the powders in the solvent followed by ultrasonication for approximately 5 minutes to assist in disassociating any powder agglomerates. A measured quantity of dispersant was subsequently added and ultrasonication continued for another 5 minutes to aid dispersion of particles. Finally, the polymer (dissolved in solvent) was added slowly to this suspension and the ultrasonication was continued for another five minutes. Once a stable suspension was obtained, films of colloidal sols were deposited on the substrates (metal-coated glass slides, Cu-foils, metal-coated FR-4) by a dip-coating method. Substrates were typically submerged in the suspension for approximately 5 seconds before they were pulled out at a rate of approximately 20 cm/min. The coated substrates were dried in an oven at 80°C to remove the solvent. This was followed by the curing treatment of the polymer at a temperature compatible with the polymer.

Since the particle size of the PMN powders was not uniform and had a wide size distribution, an attempt was made to narrow the particle size distribution using the ball milling technique. After the preparation of the powder, solvent, and dispersant mixture, the powders were ball-milled using zirconia grinding media for times ranging from 10 to 36 hours. To this mixture, a mixture of the polymer in appropriate solvent was added while simultaneously the mixture was subjected to ultrasonication. After addition of the polymer was complete, ultrasonication was continued for approximately five more minutes. The coating and subsequent curing procedures were same as that described above.

2.3. Characterization:

The microstructures of the films were characterized using scanning electron microscopy. The dielectric properties of the composite were determined by fabrication of several parallel plate structures in various areas across the substrate [3]. A Kiethley LCZ meter was used to measure the electrical characteristics. Film thickness was measured using a Tencor profilometer.

3. Results and Discussion

3.1. Characteristics of colloidal sols

A number of solvent-polymer-dispersant systems (as described in the experimental section) were studied to find optimum dispersions for each of the two types of filler powders used. It was found that the most stable suspension of barium titanate filler particles was obtained in MEK solvent with a phosphate ester as the dispersant. The optimum amount of dispersant was about 1% by weight. It was also found that epoxy was the most compatible polymer material for the above system. Sols containing PI or BCB did not make stable and homogeneous suspensions of BT fillers for any combination of dispersant and solvent used in this study.

For suspensions of PMN powders in epoxy, the best performance was obtained using oleic acid as the dispersant and MEK as the solvent. Fairly stable suspensions were also obtained with the same dispersant for BCB as the polymer and mesitylene as the solvent.

3.2. Microstructural and electrical characteristics

Figure 1 compares the microstructures of two epoxy-barium titanate composite thin films with MEK as the solvent. The film in Figure 1(a) was prepared using the conventional mixing technique while the one shown in figure 1(b) was prepared using the colloidal sol-gel technique. It is clear that the conventional mixing technique resulted in a microstructure that consisted of agglomerates of particles and voids. In contrast, the microstructure obtained using the colloidal technique is mostly free of particle agglomerates and contains very few voids. This results in an efficient packing of particles which is desirable from the point of view of achieving a high dielectric constant in the composite. Dielectric measurements indicated that the relative dielectric constant of the composite fabricated using the conventional technique was about 20 while the value for the composite prepared using the colloidal technique was about 50. This clearly indicates the critical role of the microstructure in affecting the dielectric constant of the composite. Large voids

and pores in the microstructure greatly decrease the dielectric constant of the composite due to the large volume fraction of voids that are filled with low dielectric constant material. Efficient packing of the high dielectric constant filler results in a decrease of the volume fraction of voids, and hence, an increase in the dielectric constant of the composite. For a given volume loading of the filler, a non-agglomerated microstructure would be expected to give better electrical properties since the agglomerates tend to produce voids and reduce particle packing density. It thus becomes necessary to get a good dispersion of particles for high packing density, and hence, higher dielectric constant. As evident in Figure 1(b), the colloidal sol-gel process produces a microstructure virtually free of agglomerates resulting in a higher dielectric constant in the composite.

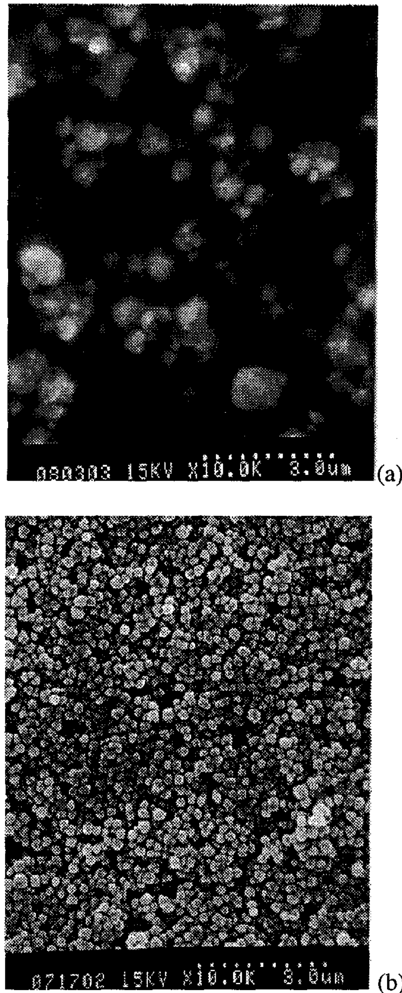

Figure 1: SEM micrographs showing the microstructures of epoxy-BT composite films prepared using (a) conventional mixing and (b) colloidal sol-gel techniques. The dielectric constant of composite shown in (a) is approximately 20 and of (b) is approximately 50.

The packing density may be further increased by introducing a bimodal distribution of particles in which finer particles can fill in the interstitial sites between coarser particles. Hence, as a next step, extremely fine barium titanate particles with an average particle size of 20-30 nm (TPL, Inc.) were mixed with the coarser barium titanate particles in a 1:5 ratio and the colloidal suspensions were prepared as described earlier. A volume ratio of fine to coarse particles greater than 1:5 led to gelling or instability in the suspensions studied here due to the high surface area of these fine particles. Figure 2 shows the microstructure of the composites prepared using the bimodal particle size distribution.

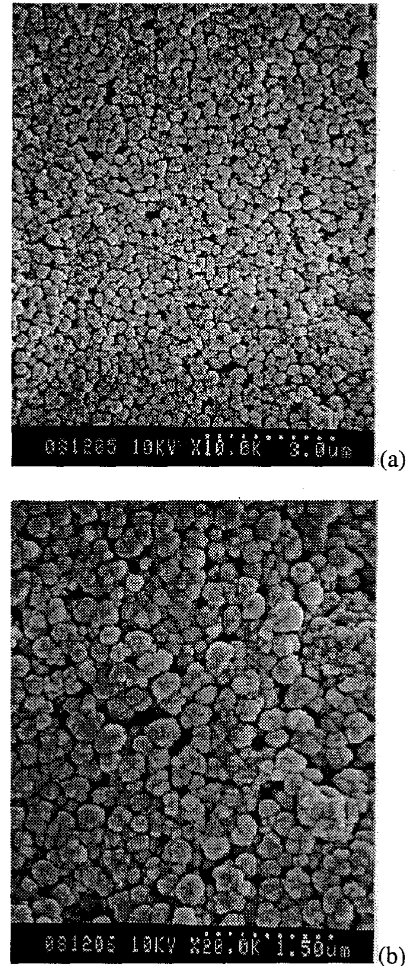

Figure 2: SEM micrographs of epoxy-BT composite films prepared by the colloidal technique and a bimodal particle size distribution. (a) Magnification equal to that of Figure 1, illustrating the difference between unimodal and bimodal particle distributions; (b) increased magnification of (a) which illustrates particles of both sizes in the composite. The dielectric constant of the composite was 74.

The particles are packed densely with the fine particles filling in the voids between coarser particles. Further, as expected, the dielectric constant value of this dense-packed composite (~74) was even higher than that prepared using unimodal particle size distribution (~50). This clearly indicates

the influence of particle size distribution on the packing density of particles and subsequently, on the dielectric properties of the composite.

Studies were also performed on preparing films from colloidal suspensions of PMN powders with various dispersants and polymers in different solvents (as mentioned in the experimental section). Figure 3 shows the microstructures of PMN-epoxy composite films prepared using MEK as the solvent and 1% oleic acid as the dispersant. The peak dielectric constant of the composite was 64. Even though the dielectric constant of PMN (~ 17,800 in sintered form) is higher than that of barium titanate, the composite films of PMN did not exhibit dielectric constants higher than 74 because the microstructure was not fully optimized..

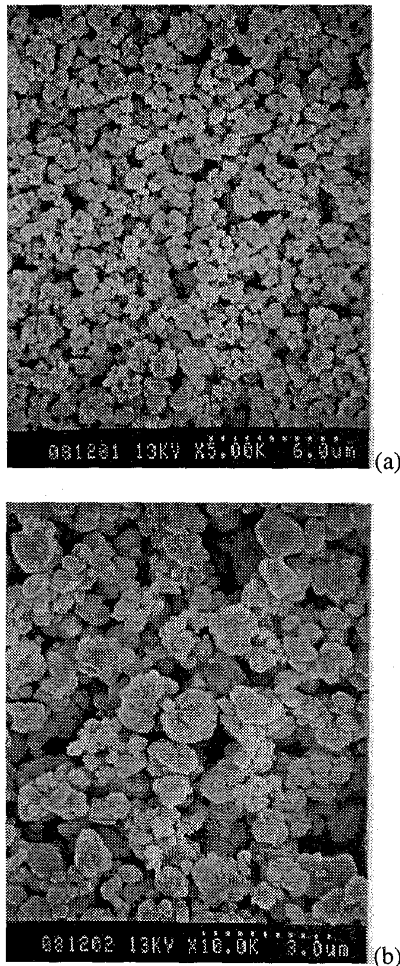

Figure 3: SEM micrographs showing the microstructure of epoxy-PMN composite films prepared using the colloidal sol-gel technique.

As can be seen in Figure 3, there are voids in the microstructure and the particles are not packed as densely as they were in the case of well dispersed and well-packed barium titanate particles (Figure 2). Thus, a combination of wide particle size distribution and insufficient dispersion resulted in insufficient packing density, and hence, a dielectric constant which is lower than expected from higher dielectric constant PMN powders. The dielectric constants of the ball-milled (and dispersed) PMN-polymer composite films were similar to those prepared without ball milling. Hence, the availability of PMN powders with a more uniform particle size distribution and of better dispersants for the PMN-polymer-solvent system are areas of future exploration

3.3. Film Deposition on Large Area Substrates:

Dip coating was used in the above characterization of the colloidal films; however, in packaging applications, especially on patterned or textured substrates, an alternative approach is desirable. Meniscus coating of thin films resembles dip-coating and was used in studying thin film deposition on large area substrates. The major advantages of meniscus coating are: (i) low wastage of material, (ii) ease of deposition of thin films on large area substrates; and (iii) applicability to a wide variety of substrate materials. A detailed description of meniscus coating of thin films is given in ref. [12].

Epoxy (SU-8) dissolved in MEK-solvent with $BaTiO_3$ particles (0.1 μm) and a phosphate ester dispersant was used in meniscus coating experiments. A volume loading of 52 % was used for the first studies. Ultrasonication of the colloid was carried out immediately prior to loading the composite mix in the meniscus coater and ultrasonication was not carried out during film deposition. No settling of the particles was observed over a five-hour period.

Thin films were deposited on Cu-cladded PWB substrates. A simplified schematic of the capacitor fabrication on large area PWB substrates is shown in Figure 4. A slot-type applicator tube was used in the film deposition. Further, no heating of the substrate was required during deposition due to the low boiling point of the MEK solvent. Slow speed and multiple passes (two passes for the films described here) are required to achieve films with good uniformity and desired thickness. One pass can be used to achieve the desired thickness with viscosity control of the composite mix. However, this proved to be a difficult parameter to vary widely since for the suspensions studied has the best final film properties were obtained from dispersions of low viscosity.

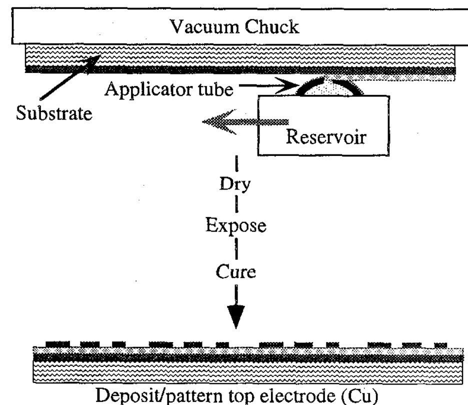

Figure 4. Large area nanocomposite capacitor fabrication

Upon deposition, the film was dried, UV-exposed (since the material is negative-working photosensitive), and cured at 160 °C for 2.5 hours in an oven with air ambient. A top copper electrode was deposited and patterned using standard photolithographic processing. The board was populated with many parallel plate capacitor structures with varying top electrode area (1.54, 0.28 and 0.096 cm^2). The capacitance and loss of these capacitors were measured at 100KHz using a Kiethley LCZ-meter. The average specific capacitance across the board of good (non-shorted) capacitors was 9.9 nF/cm^2 (dielectric thickness ~3 μm) and the capacitance variation across the substrate was less than 8%. The ratio of the number of good capacitors to the total number of capacitors for three different capacitor areas were as follows: 5/36 for 1.54 cm^2, 44/150 for 0.28 cm^2 and 85/185 for 0.096 cm^2. No micro-cracks were observed under an optical microscope, thus suggesting that the shorts were largely due to the rough surface (typically 2 - 3 μm) of the Cu-laminate. Typical behavior of the capacitance and loss-tangent of the capacitors on this board as a function of frequency and temperature are shown in Figure 5.

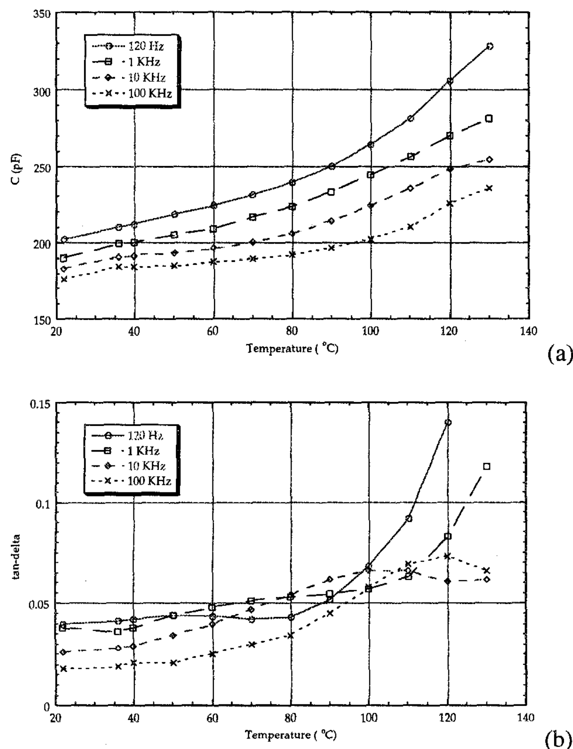

Figure 5. Typical capacitance (a) and loss-tangent (b) behavior as a function of frequency and temperature of capacitors fabricated on PWB substrates using meniscus coating from colloidal suspensions.

This was carried out by fabricating smaller structures (silver paste as the top electrode) on the same board to avoid LC resonance in the frequency of interest. This measurement indicates stable dielectric properties of the composite at lower temperatures as a function of frequency as well as low dielectric loss in this range. At higher temperatures the material becomes lossy and also capacitance increases significantly. This is possibly related to the thickness of the film (extremely thin at local spots due to surface roughness of the board) inducing large leakage currents and also due the addition of dispersants affecting the electrical properties. This requires further investigation.

5. Preliminary Conclusions and Future Work:

This paper illustrated the processes involved in the development of a filled-polymer composite with high dielectric constant for thin-film deposition on large area PWB substrates. Dielectric constant as high as 70 can be achieved with an epoxy-$BaTiO_3$ combination. Colloid composites and meniscus coating were found to be quite compatible in achieving films of high dielectric constant values on large area PWB substrates. Specific capacitance of 9.9 nF/cm^2 on Cu-laminate PWB substrate was achieved. These combined systems, when developed further, will allow integration of large specific capacitance values on large area substrates. Future work will involve further characterization of these films as well as attempts to further increase the dielectric constant and reduce solvent usage.

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