Processing and Dielectric Properties of Nanocomposite Thin Film "Supercapacitors" for High-Frequency Embedded Decoupling

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Abstract—The embedded decoupling capacitor problem has been pursued by several groups and industry around the world over the past decade. Currently, popular ceramic-polymer composites can only provide limited capacitance, typically within 10 nF/cm ^{2}. With the reliability and processing constraints imposed, the capacitance density would be much lower. Newer capacitor concepts such as supercapacitors can overcome the limitations of existing polymer based capacitors and are now being considered. These concepts rely on nanostructured electrodes for high surface area per unit volume resulting in ultrahigh capacitance densities and unconventional polarization mechanisms such as electrical double layer and interfacial polarization.

Supercapacitive structures lead to ultrahigh capacitance densities of the order of hundreds of microfarads. However, manufacturers report that the properties are unstable at high frequencies, typically even at tens of megahertz. To adapt these structures for mid-to-high-frequency decoupling, it is hence essential to systematically characterize the high-frequency dielectric properties of the thin nanocomposite films and nanostructured electrodes. This paper reports complete electrical characterization of a part of such a system, carbon black-epoxy nanocomposites. The high-frequency properties of the cured films were evaluated with a multiline calibration technique by measuring S-parameters of transmission lines fabricated on the top of the dielectrics. Though the nanostructured carbon black epoxy composites showed high dielectric constant of 1000 at low frequencies, the high frequency (0.5–4.5 GHz) dielectric constant was found to be only up to 10 times that of the base polymer matrix. The measured dielectric constant at gigahertz frequencies increased from 15–30 when the filler content was increased from 3.8% to 6.5%, with excessive leakage currents. Based on these measurements, conduction and polarization relaxation mechanisms will be assessed and the suitability of the thin film supercapacitors for high-frequency decoupling applications will be discussed.

Index Terms—Integrated circuit (IC), printed wiring board (PWB).

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I. INTRODUCTION

AS integrated circuit (IC) technologies move toward higher power densities, clock frequency, and lower voltages, power integrity in the IC-package will be one of the most challenging issues the microelectronic industry will face. Surface mount ceramic components, which are the current workhorse of the electronics industry, are bulky, expensive, and not suitable for high-frequency decoupling above a few hundred megahertz because of their excessive lead inductance. Industry is now moving toward embedded passive components for superior system level performance compared to the surface mounts used in today's systems. In order to address the power integrity problem in high-speed microprocessors, there is an urgent need for integrated thin film high dielectric constant capacitor components.

The operating voltage, power, and frequency for high-performance microprocessors are predicted by ITRS to be 0.9 V, 170 W, 3–4 GHz in 2005 and 0.6 V, 210 W, 5–8 GHz in 2010 [1]. Microprocessors are designed with lower voltage requirements in order to reduce overall power dissipation. Lower voltages require power supplies with much higher current capabilities, up to three times that of previous microprocessors, with correspondingly higher load-change transients. Impedances of power distribution systems monotonically increase in the frequency domain due to the inductive effects with several resonance peaks caused by the capacitive loops leading to dynamic voltage fluctuations. Decoupling capacitors act as reservoirs of charge and supply the transient currents for switching circuits, thereby isolating the parasitic inductance of the power network and minimizing switching noise. However, impedance of each capacitor branch, and the conductors necessary to connect the components, limit the capacitor current. Consequently, it becomes important to 1) design conductor paths using wide (low inductance) tracks, 2) locate decoupling capacitors as close as possible to the fast switching load device, and 3) increase the capacitance.

The rise/fall switching transition is very short in the IC, has the medium duration in the package, and longer duration on the printed wiring board (PWB) [2]. Both bulk and high-frequency bypass capacitors are used today because of the relatively slow speed at which a power supply (or a dc-to-dc converter) can react. For example, a microprocessor's current transients are on the order of 1–20 ns while a typical voltage converter has a reaction time of 1–100 μs. Therefore, new design

will require 1) high-frequency decoupling capacitors very close to it to minimize the series inductance and resistance, 2) mid-frequency decoupling capacitors on the package, and 3) low-frequency/high-capacitance decoupling capacitors on the PWB.

The embedded decoupling capacitor problem has been pursued by several groups and industry around the world over the past decade. Initial research mostly focused on composite thin films consisting of high dielectric constant ceramic particles in a low dielectric constant polymer matrix. For ceramic-polymer composites, the modified Lichtenecker's law [3], commonly used to predict the effective dielectric constant of polymer-ceramic nanocomposites with different volume fractions, can be written as

$$\log\varepsilon_c = \log\varepsilon_m + (1-k)v_f\log\left(\frac{\varepsilon_f}{\varepsilon_m}\right) \qquad (1)$$

where $\varepsilon_c, \varepsilon_m$ and ε_f are dielectric constants of nanocomposite, matrix, and ceramic filler, respectively, v_f is volume fraction of ceramic filler, and k is a fitting constant subject to the composite material. These filled polymers, however, can only provide limited capacitance, typically within 10 nF/cm^2 [4], [5]. The adhesion strength of a epoxy-barium titanate nanocomposite with copper reduces from 6–8 MPa at 20% filler to less than 2 MPa at higher filler content. With the reliability and processing constraints imposed, the capacitance density would be much lower. High K ferroelectric powders exhibit an intrinsic high-frequency relaxation behavior that gives rise to frequency dependent dielectric constant and loss. The dielectric relaxation frequency is inversely related to the ratio of domain size and shear wave velocity, and typically varies from 100 MHz to 10 GHz. The resulting high-frequency dielectric loss increases with the volume of the ceramic component, exceeding the dielectric loss of the individual components.

Nanocomposite "Supercapacitor" approach: Newer capacitor concepts such as supercapacitors and nanocapacitors can overcome the limitations of existing polymer based capacitors and are now being considered. These concepts rely on nanostructured electrodes for high surface area per unit volume resulting in ultrahigh capacitance densities and unconventional polarization mechanisms such as electrical double layer and interfacial polarization. Fillers such as carbon black, when dispersed in a polymer, were shown to achieve high capacitance and effectively higher dielectric constant of the order of thousands, presumably from the giant interfacial polarization and effective increase in the electrode surface area from the nanometallic particles [6]. While several studies were reported on nanodielectrics with insulating fillers such as titania, silica, barium titanate, etc. [7] very few studies were reported on nanodielectrics with conducting fillers for decoupling capacitor applications.

Incorporating conducting fillers leads to orders of magnitude increase in the dielectric constant, which is usually attributed to the higher electrode surface area that extends into the bulk of the dielectric. The effective surface area dramatically increases as the percolation limit is approached. There are no accurate models to capture the dielectric behavior of nanodielectrics with conducting fillers. For a metal filled conductor-insulator system, its high dielectric constant near critical filler loading is explained by the percolation theory [8], [9]. According to
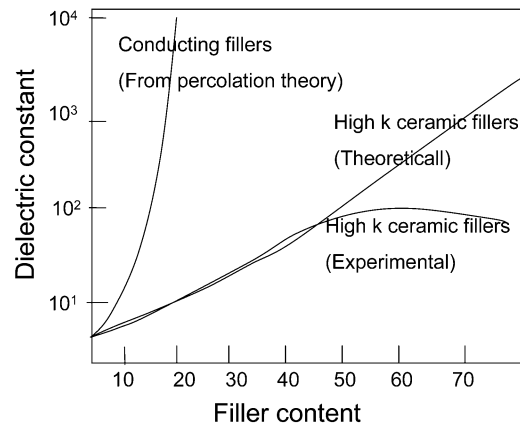

Fig. 1. Dielectric constant of polymer composites with metal and ceramic fillers. With the ceramic fillers, the dielectric constant saturates beyond certain filler content. The optimal filler content can be increased with improved filler packing density (using bimodal or multimodal particle size distribution).

the percolation theory, the dielectric constant of a percolation system exhibits a power-law behavior, which can be expressed as

$$\varepsilon = \frac{\varepsilon_{\mathrm{matrix}}}{(f_c - f)^s} \qquad (2)$$

where f_c is the percolation volume fraction dependent on the filler dispersion, size, shape, etc., f is the actual volume fraction ,and s is a scaling constant dependent on material properties, microstructure, and connectivity of the metal-insulator. Incorporating metallic fillers can result in extremely high dielectric constant at much lower filler loading as shown in Fig. 1. However, the high dc leakage, dielectric loss, and low breakdown strengths prevented the application of these materials systems for high density capacitors. In addition, the high dielectric constant resulting from interfacial polarization is not shown to be stable in the high-frequency range, as reported by three independent studies [10]–[12]. High-frequency measurements of carbon black epoxy nanocomposites have shown that the dielectric constant reduces from 10^3 at 10 kHz to less than 10^2 at 100 MHz.

Double layer supercapacitors are based on anions and cations separated in an electrolyte (Fig. 2). Energy is stored in an electrochemical capacitor by charge separation within the micro/nano pores of a large surface area electrode material. The charge separation is distributed throughout the volume of the electrode material in the double layer formed at the electrode/electrolyte interface. Current supercapacitors can achieve hundreds of microfarads, but these are not available in planar format and are not suitable for embedded decoupling. The conducting network is typically made up of activated high-surface carbon. Though not expected to be stable at gigahertz frequencies, invoking supercapacitive structures with high surface area electrodes and double-layer/interfacial polarization with nanometallic electrodes and thin electrolytes can yield capacitance higher than 100 μF/cm^2 per single layer.

To adapt "supercapacitive" structures for mid-to-high-frequency decoupling, it is hence essential to systematically characterize the high-frequency dielectric properties of the thin nanocomposite films and nanostructured electrodes. This work
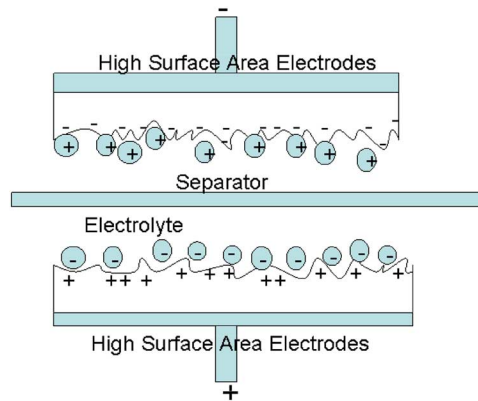
Fig. 2. Structural schematic of a double layer supercapacitor.

Fig. 3. Nano carbon black-PGMEA dispersions with different dispersants. Optimized dispersant content can be estimated from these curves.

investigates the high-frequency characteristics and dc leakage behavior of supercapacitive carbon black-polymer composites and their suitability for embedded decoupling.

II. PREPARATION OF NANOCOMPOSITE FILMS

The nanocomposite films were fabricated by dispersing conducting carbon black (Vulcan XC-72R, Cabot Corporation) in a polymer compatible solvent with a suitable amine-based surfactant. To improve the processability of the nanodispersions and obtain a homogeneous film with minimal defects, it is essential to minimize the aggregation of carbon black leading to lower viscosity dispersions. Dispersion of nanoparticles in a medium requires repulsive forces to be generated between the particles in order to overcome the London–Vanderwaals forces that lead to aggregation. Colloids in nonaqueous media are generally believed to be stabilized by steric hindrance of the adsorbed polymer layers on the colloid surface. The steric stabilization mechanism by itself is usually not strong enough to promote good dispersion at high solids loading. It has been shown in many systems that surface charge originates on particles even in aprotic or low-polarity solvents. Charge-generation is generally attributed to the acid-base type chemical interactions between solvent, particles, and dispersant. The three-way interactions between particle, solvent, and dispersant can be better explained by quantifying their acidity and basicity. Studies show a direct correlation between high zeta potential and low viscosities even in nonaqueous systems, hence establishing the role of electrostatic repulsions. Repulsive forces can also be created by a combination of electrostatic forces from the electrical double layer and steric hindrance (electrosteric). Fowkes *et al.*[13] studied the dispersion of carbon black in nonaqeuous systems. They proposed that the stabilization of carbon black suspensions occurs by mechanism stabilization in three steps: adsorption of undissociated molecules onto the solvent via acid-base interactions, dissociation of adsorbed molecules on the particle, and desorption of anions in to the solution. From detailed studies, Fowkes *et al.* concluded that the charge-generating process involves proton transfer from acidic sites on the particle surfaces (carbon black has a pH varying from 5–6) to adsorbed basic dispersant molecules followed by desorption of the dispersant cation. The rate of desorption is only appreciable when excess dispersant is left
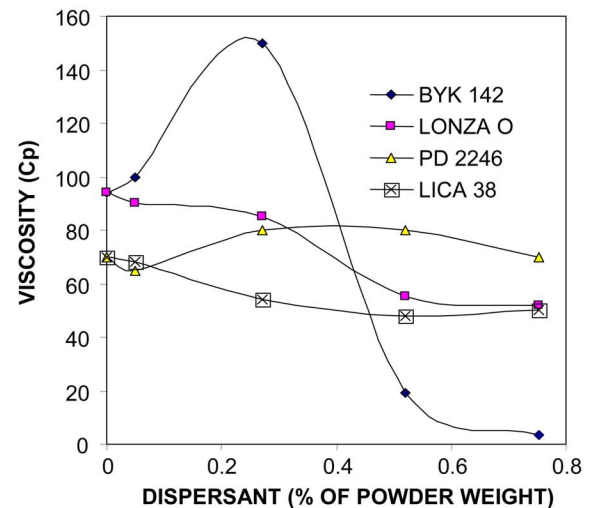
in the solution and this process is most efficient with large dispersant molecules or micelles. Studies with the C-14 tagged basic dispersants and tritium tagged acidic dispersants proved that each desorbed dispersant carries one proton into solution. Similar electrostatic phenomena were observed with a wide range of dispersants in nonaqueous polymer solutions.

In this study, various dispersants were evaluated to prepare the carbon black dispersions in propylene glycol methyl ether acetate (PGMEA) because no reports on this system were found in the literature. The efficacy of a dispersant can be evaluated from the rheological studies (CPE LVDV-I+, Brookfield Engineering Laboratories, Inc., Middleboro, MA). Dispersant Byk-142 was found to be the best dispersant from the viscosity measurements. Other dispersants (Lica 38—alkoxy titanate; Lonza C-Imidazoline based; PD 2246—Poly ethoxy amine) did not provide significant changes in the suspension viscosity. The dispersant byk-142 consists of an alkylated polyamine with mainly tertiary aminogroups. The molecular weight of this strongly basic building block is relatively high and has dense packing of the aminogroups. The aminogroups are then neutralized with a polar phosphoric acid ester forming a salt. The minimum in viscosity occurs when the weight ratio of dispersant/powder of the dispersant reaches 0.7, beyond which the dispersant was not effective in further lowering the viscosity (Fig. 3). This fraction was used in the subsequent studies to prepare the suspensions.

Zeta potential studies indicate the stabilization mechanisms of nano carbon black. Suspensions with different dispersant concentrations were analyzed using a Coulter Delsa 440 SX (Beckman Coulter, Inc., Fullerton, CA). The sample cell was cleaned and calibrated with mobility standard before each set of measurements. High solids loading suspension samples were found to be susceptible to multiple scattering and interaction errors. The dilution of the samples was adjusted to obtain reproducible values. The instrument uses specific conductivity and the measured electrophoretic mobility data to calculate the zeta potential at the surface of the particles. These measurements are highly sensitive to the ambient temperature. Hence,
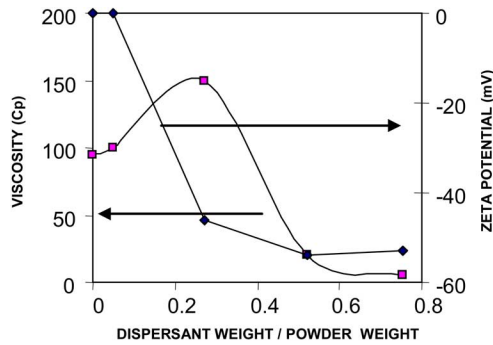
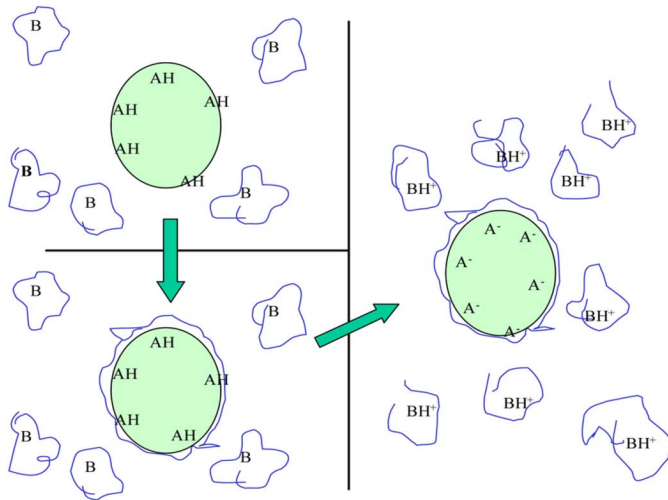Fig. 4. Viscosity and zeta potential measurements of CB–PGMEA suspensions.

TABLE I
FORMULATION OF CB-POLYMER NANOCOMPOSITES

Wt of Carbon black suspension (6 wt. % in PGMEA)	Epoxy (55 wt. % in PGMEA)	BCB (46 vol. % in mesitylene)	Filler content (Vol. %)
2.81	10	x	2
5.5	10	x	3.84
9.5	10	x	6.45
5.5	x	10	3.88
9.5	x	10	6.52

Fig. 5. Electrosteric stabilization mechanism in carbon black-PGMEA suspensions with an alkyl amine (Byk-142) dispersant.
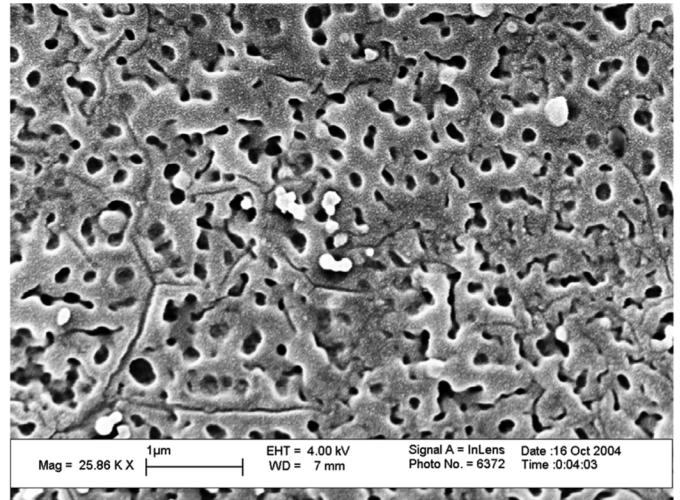
Fig. 6. Top surface of the carbon black-epoxy nanocomposite films (5.5–6.5 μm thick).

each sample was allowed to equilibrate to the temperature of the cell jacket (25 °C) before taking the measurement. At high dispersant concentrations, carbon black develops $-ve$ charge leading to electrostatic repulsive forces through the electrical double layer interaction, thereby lowering the viscosity. The negative surface potential measured in this work (Fig. 4) is in agreement with the mechanism suggested by Fowkes *et al.* [13] (Fig. 5). Higher viscosity was observed at low dispersant contents. Similar electrosteric stabilization was also reported with BaTiO$_3$ in nonaqueous solvents using phosphate ester as the dispersant [14], [15]. Some of these dispersants may not be compatible with certain polymers, which may constrain the use of the dispersant.

Carbon black suspensions in PGMEA were ball-milled for 24 h using Byk-142 dispersant. The suspension had 6.0–6.5 wt.% (roughly 3.5 vol.%) of carbon black. Two polymers, epoxy (LMB 7081, Vantico Corporation, obtained as 55 wt.% epoxy in PGMEA) and BenzoCyclo Butene (cyclotene 3022–46, obtained as 46 vol% in mesitylene from Dow Chemicals) were used as the matrix for the nanocomposites. Different amounts of polymers were added to make the nanocomposites with varying filler contents (Table I). Curing was done at 160 °C and 250 °C, respectively, for the epoxy and BCB. The suspensions were spin-coated to yield two sets of film thicknesses—one with 3.5 μm and the other with 5.5–6 μm. The addition of epoxy led to the aggregation of the carbon black (Fig. 6) while the BCB addition retained the low viscosity and suspension stability. The microstructures are compared in Figs. 6 and 7. The electrical behavior of these composites with different microstructures is compared in the following sections.

III. ELECTRICAL CHARACTERIZATION

Electrical measurements were done in low-frequency–high-frequency ranges (5 Hz–5 GHz) with three different instruments. The low-frequency measurements were done with an HP 4192 A LF Impedance Analyzer. The instrument is capable of measuring L, C, R and impedance from 5 Hz to 10 MHz. Measurements in the range of 100 kHz to 5 MHz were done with a Precision LCR meter (HP 4285A). The high-frequency measurements were conducted with a S-parameter Network Analyzer (HP Model 8720 ES). All these measurements were done without any dc bias.

Though the dielectric constant was measured to be 1000–10 000 at low frequencies (Fig. 8), as shown in previous studies [10]–[12], the dielectric constant quickly drops to less than 100 at megahertz. The dielectric constant increased with the filler content as expected (Fig. 9). The dielectric constant steadily decreases with increasing frequency as seen with all the three instruments. The sharp fall in dielectric constant at lower frequencies agrees with earlier observations [10], [12].
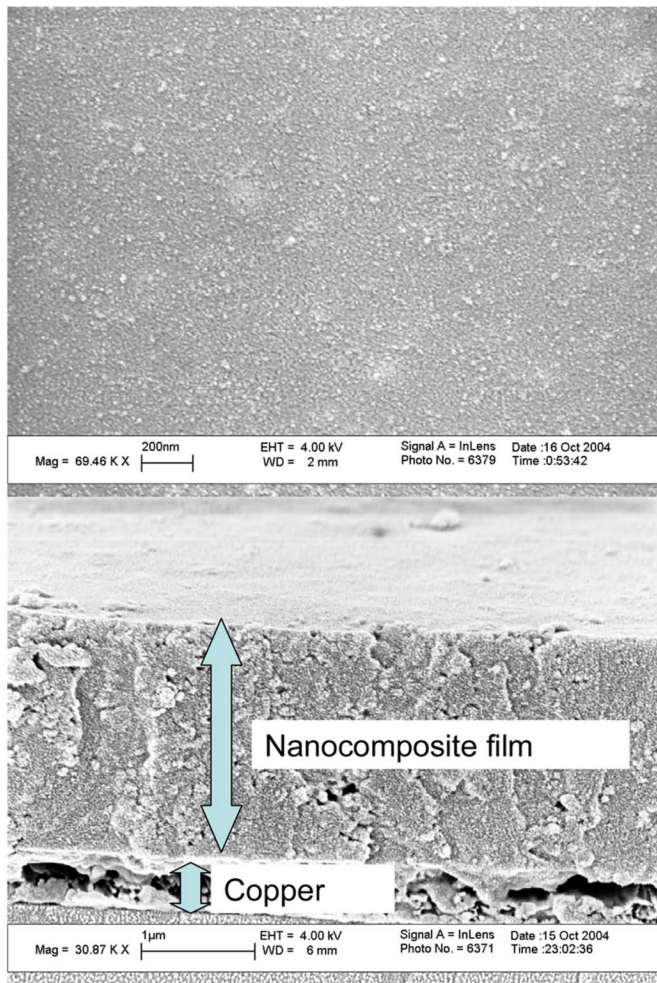
Fig. 7. Top and cross section (fractured/unpolished) of the carbon black-BCB nanocomposite films (4–4.5 μm thick). Note that these films are much more homogeneous at a finer scale compared to the carbon black-epoxy films.

Fig. 9. Low-frequency measurements (LCR meter) of carbon black-epoxy composites with different filler contents.

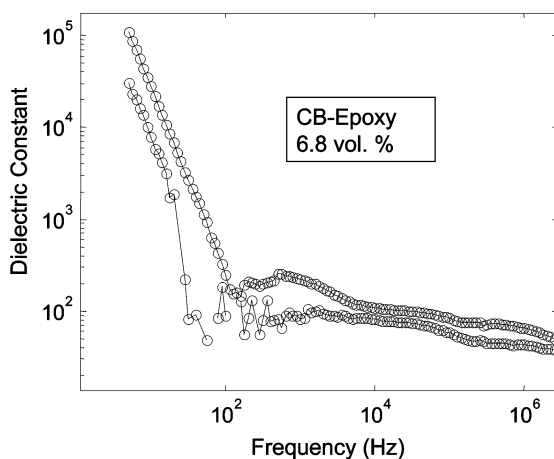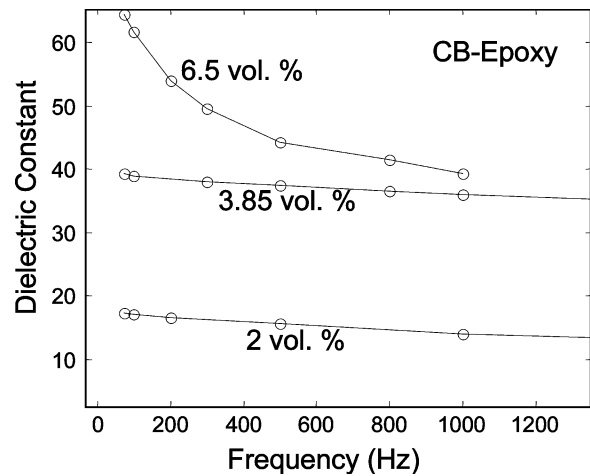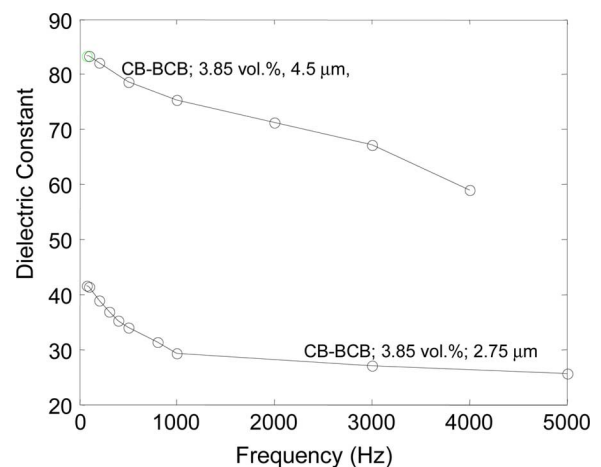Fig. 10. Dielectric constant comparison between thin and thick carbon black-BCB composites.

Fig. 8. Low-frequency measurements (5 Hz–5 MHz) using a impedance analyzer. The two curves represent two devices from the same sample.

Similar studies with titania-polymer nanocomposites showed relaxation at less than 10 Hz [16]. It could be possible to push this frequency to megahertz by improving the dispersion, choosing finer conducting particles with higher conductivity,

and preventing charge leakage by an insulating layer around the metallic particle.

With BCB composites, the dielectric constant was much higher for thicker films compared to thinner films (Fig. 10). This indicates that it may be essential to characterize the dielectric constant as a function of thickness in order to understand the complete capacitance behavior of the composite. Thickness effects can be indirectly inferred by measuring capacitance with dc bias. A external dc bias adapter (Agilent 16065 C) was used to apply a voltage in conjunction with the LCR meter. The capacitance for agglomerated carbon black-epoxy composites marginally decreased by 3%–5% until a field strength of about 0.4 V/μm (up to 3 V for an 8 μm film) but increased later as the field strength reaches 1 V/μm. For carbon black-BCB composites, the capacitance continuously decreased by about 12% as the voltage bias was increased to 1 V/μm (3.5 V for a 3.5 μm thick film). For epoxy composites, voltage increases the interfacial polarization leading to higher capacitance while for BCB composites, the capacitance continuously decreases with the voltage because the leakage current becomes predominant with voltage increments.

The dielectric loss of CB-epoxy composites with low (2 vol.%) and medium filler content (3.85 vol.%) increased from 0.05 at 100 kHz to 0.3 at 2 MHz. The dielectric loss for high filler content (6.5 vol.%) steadily decreased from 0.35 at 75 kHz to 0.2 at 3 MHz indicating a relaxation process at even kilohertz frequency. The dielectric loss for well-dispersed CB-BCB composites was much higher (0.5–0.8) between 100 kHz–2 MHz and did not show any systematic trends. It is clear that the loss is dominated by the low resistance. The percolation threshold, where the material switches from dielectric to conducting behavior, depends on the structure of the nanocomposite. For 6 vol.% filler content, well-dispersed CB-BCB did not show any capacitive behavior while the aggregated CB-epoxy showed high dielectric constant. Literature reports percolation threshold varying from 0.04 % (for nanotubes-polymer composites) to 10 vol.% (carbon black-epoxy), depending on the size, shape, and distribution of the filler in the nanocomposite.

A. High-Frequency Characterization

The dielectric constant of the films from 100 MHz to 8 GHz was estimated using a multiline CPW method. Coplanar waveguides of different lengths were fabricated on the nanocomposite films (Fig. 11). The dielectric constant and loss were extracted from S-parameters as described in [17] and [18]. This technique enables to accurately deembed the dielectric constant from the effective propagation constant calculated from the S-parameters. The use of multiline technique eliminates the errors associated with the impedance mismatch [19], [20]. The propagation factor (γ) of a transmission line structure on a dielectric can be calculated from the S-parameters measured on CPW lines of different lengths

$$\gamma = \frac{a\cosh\left(\frac{1}{2}\mathrm{Tr}(M_1 M_2{}^{-1})\right)}{\Delta L} \qquad (3)$$

where ΔL is the difference in length of the CPW lines, and M_1 and M_2 are ABCD matrices for different lengths. *Tr* refers to the trace of the matrix. γ can also be expressed as

$$\gamma = \sqrt{(R + j\omega L)(G + j\omega C)} \qquad (4)$$

where $R, L, G,$ and C are, respectively, the resistance, inductance, conductance, and capacitance per unit length of the transmission line. Since dielectric and metallic losses cannot be separated using measurements made on the unknown material alone, identical structures were fabricated on a pure BCB film with the same thickness. The dielectric constant and loss are well-characterized for BCB and are 2.7 and 0.0008. Applying (4) to the nanocomposite and BCB

$$\frac{\gamma_1}{\gamma_2} = \frac{\sqrt{(R_1 + j\omega L_1)(G_1 + j\omega C_1)}}{\sqrt{(R_2 + j\omega L_2)(G_2 + j_2\omega C_2)}}. \qquad (5)$$

The CPW structures on the nanocomposite and BCB were identical and both have a permeability of 1. Therefore, the equation reduces to

$$\frac{\gamma_1}{\gamma_2} = \frac{\sqrt{(G_1 + j\omega C_1)}}{\sqrt{(G_2 + j\omega C_2)}} \qquad (6)$$
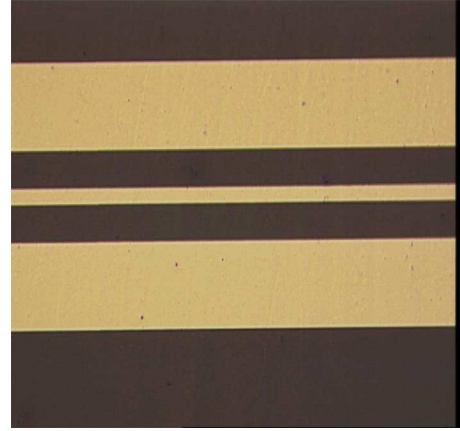

Fig. 11. 250 μm pitch CPW transmission lines fabricated on carbon black composite films.

where G is associated with the loss tangent. C and G are the effective capacitance and conductance of the transmission line and can be related to the dielectric properties [19]

$$C = 2\epsilon_0(F_{\mathrm{upper}} + \varepsilon F_{\mathrm{lower}}) \qquad (7)$$
$$G = 2F_{\mathrm{lower}}\omega\varepsilon\tan(\delta). \qquad (8)$$

The ratio $F_{\mathrm{upper}}/F_{\mathrm{lower}}$ is a geometrical factor that can be calculated from the measurements with two samples of known properties having the same geometries

$$\frac{\gamma_1}{\gamma_2} = \sqrt{\frac{2j\omega\varepsilon_0\left(F\mathrm{upper} + \varepsilon_r^1 F\mathrm{lower}\right) + 2F\mathrm{lower}\omega\varepsilon_r^1\tan(\delta)_1}{2j\omega\varepsilon_0\left(F\mathrm{upper} + \varepsilon_r^2 F\mathrm{lower}\right) + 2F\mathrm{lower}\omega\varepsilon_r^2\tan(\delta)_2}} \qquad (9)$$

where γ^1 and γ^2 refer to the propagation constants when the CPW lines are fabricated on material 1 and 2, respectively, both with known properties.

From these equations, the dielectric constant and loss tangent of the nanocomposite films can be calculated. In this work, F_{upper} is assumed to be much smaller than F_{lower}. In other words, capacitance per unit length of the transmission line is dominated by the material underneath and is assumed to be proportional to the permittivity of the material.

The scattering parameters were measured using an S-parameter Network Analyzer (HP Model 8720 ES). The probes were calibrated using Open, Short, and matched 50 Ω structures on an aluminum oxide substrate. Though the nanostructured carbon black epoxy composites showed high dielectric constant of 100–1000 at low frequencies (100 Hz–1 kHz, measured with a LCR meter), the high-frequency (0.5–4.5 GHz) dielectric constant was found to be much lower (Fig. 12). The measured dielectric constant at high frequencies increased only from 12–25 at higher frequencies when the filler content was increased from 3.85% to 6.5%, while the difference between various filler contents was more dramatic at lower frequencies. At high frequencies, the dielectric constant gradually drifted down to lower values.

The dielectric loss of nanocomposite films with conducting fillers is much higher than ceramic-polymer composites. The loss is 0.08–0.1 for 2 vol.% filler CB-epoxy and 0.2–0.3 for 3.85
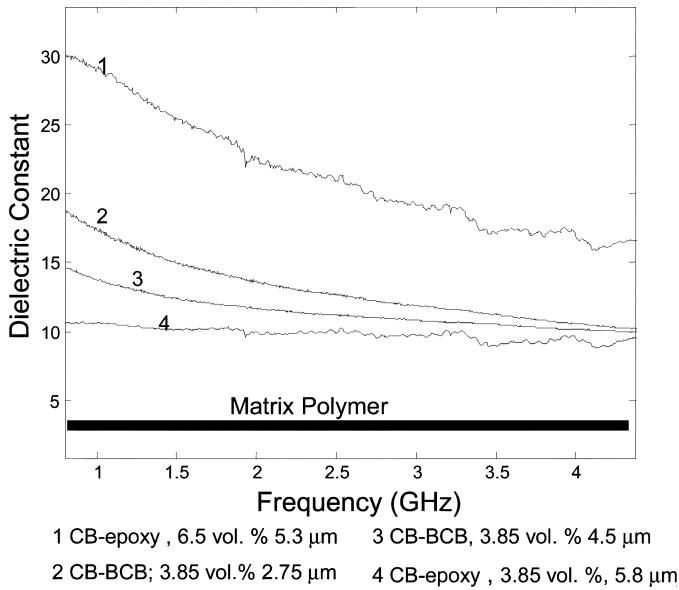
Fig. 12. High-frequency characteristics of carbon black-polymer nanocomposite thin films extracted from the S-parameter measurements.

1 CB-BCB, 6.5 vol. %; 4.5 μm 4 CB-Epoxy , 6.5 vol.%, 5.3 μm
2 CB-BCB; 3.85 vol.% 4.5 μm 5 CB-Epoxy , 3.85 vol. % 5.8 μm
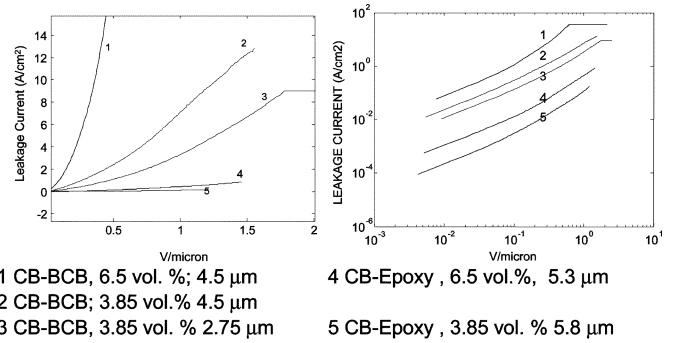3 CB-BCB, 3.85 vol. % 2.75 μm

Fig. 13. Leakage current measurements of CB nanocomposites with different formulations, as a function of electric field strength. Both log–log and linear scales are shown here.

IV. DISCUSSION

The metal-insulator contact gives rise to an equivalent circuit with interfacial polarization, a quantity that is orders of magnitude larger than the geometrical capacitance of the insulator film. With metal-electrolyte films, the value could be much higher because of the double-layer capacitance. The resulting increase in capacitance is shown to be higher by a factor of $10^3 - 10^5$. This can potentially lead to a capacitance density of 100 μF/cm^2 even when the film thickness is few microns. However, the enhancement decreases with increasing frequency. When the frequency becomes larger than the inverse time of ion migration through the solid-electrolyte, the counter charge has no time to react to the charge variation in the metal leading to Lorentzian shape of the dielectric permittivity of the frequency dependence [10]. For double-layer capacitors, the relaxation frequency is dependent on the time needed to charge the double-layer via migration of ions through the bulk of the electrolyte to the interface. Hunter *et al.* express this as [23]

$$\tau = \frac{2\pi t k \varepsilon_0}{\kappa \delta} \qquad (10)$$

where t is the separation between the electrodes, κ is the electrolyte ionic conductivity, k is the dielectric constant, ε_0 is the permittivity of free space, and δ is the double layer thickness. Good ionic conductors (superionic conductors) and thin electrolytes can enable megahertz of bandwidth according to (10).

For the CB-polymer composites, the conducting network in contact with the electrode increased the plate surface and the isolated conducting particles contribute to the interfacial polarization leading to an effective increase in permittivity (Fig. 14). A major contribution to the relaxation is the RC-ladder effect arising from the high equivalent series resistance (ESR) in the conducting network. This is also usually seen in the tantalum capacitors. Another contribution to the observed relaxation process for metal-insulator composites is attributed to the restricted motions of the charge carriers. The breadth of the frequency window where this polarization effect would be observed is discussed in few studies before. Ardi *et al.* [11] estimate the relaxation time varying from seconds to microseconds, depending on the ratio of the composite conductivity and permittivity (σ/ε). More detailed analysis by Bowler and Youngs [24], [25] also show the effect of filler conductivity and its dimensions on the relaxation frequency. Finer particles with

vol.% CB-epoxy estimated from the high-frequency measurements. Similar numbers were also measured at low frequencies.

The leakage currents were measured with a dc parameter analyzer (Hewlett Packard, Model 4155). The values are higher with well-dispersed carbon black in BCB, where the microstructure is homogeneous at even 100 nm scale (Fig. 13). The plots on log-log scale approximately follow the power law/child's law ($I \alpha V^m$) with the exponent m varying from 1.1–1.4. Well-dispersed carbon black leads to higher exposed surface area and more charge storage in the nanocomposite. However, the leakage current is also much higher for the same composites because of improved dispersion. The nanosized conducting particles form a network leading to high leakage even at low filler contents. A resistance exists at the contact area between the conducting particles. This is a consequence of the current flow being constricted through small conducting spots. The tunneling resistance is exponentially dependent on the insulating film thickness between the conducting particles and is also sensitive to the potential barrier height and shape. The potential barrier depends on the work function for electron emission from metal into the material and the permittivity of the film. The studies of Li and Morris [21] show the effect of contact resistance on the total composite resistivity. The leakage current for the CB-epoxy nanocomposites that are much more aggregated was lower compared to CB–BCB nanocomposites for the same filler content. Since the filler is nanodimensional (20–30 nm) with ultrahigh surface area, it would be difficult to prevent leakage unless the particles themselves are insulated. An acceptable leakage current may limit the filler content to a value much below the percolation threshold. Improved dispersion leading to finer nanoparticle aggregates, while improving the dielectric constant also increases the leakage current. The trends in the graphs indicate that certain aggregation may benefit the overall capacitor performance unless the conductor particles themselves are insulated (for example, Al/Al$_2$O$_3$, [22]).
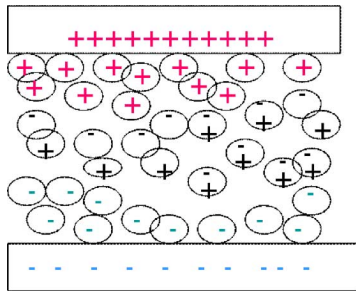
Fig. 14. Schematic of the polarization scheme for highly networked conducting carbon black based nanocomposites.
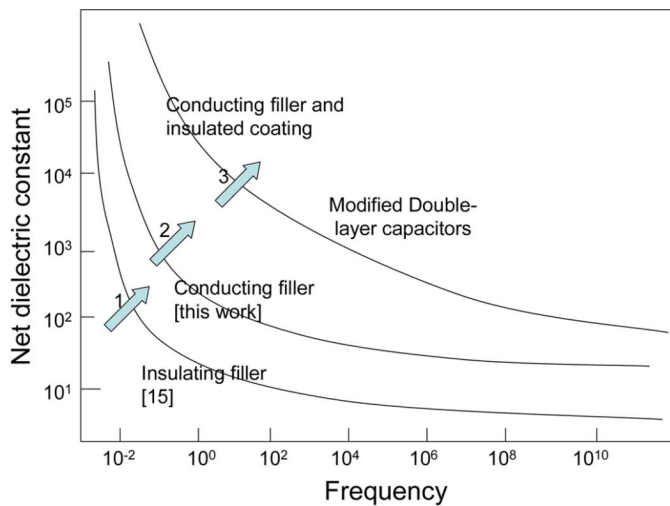

Fig. 15. Schematic variation of nanocomposite dielectric constant with frequency, predicted from this work and literature. Arrow 1: With high K insulating fillers; Arrow 2: With higher conductivity fillers; and Arrow 3: With superionic conductors and nanostructured electrodes.

improved conductivity can retain the polarization at higher frequencies. Bulk of interfacial polarization in CB-polymer system is typically stable in the range of 100–1000 Hz, which is of not much practical value for embedded decoupling applications. From these high-frequency measurements, it is evident that certain amount of polarization is retained even at gigahertz frequencies. The dielectric constant for these polymer composites is not as high as that of many perovskite ceramics like barium titanate/strontium titanate but can provide simpler organic compatible decoupling solutions for some applications. Though a direct correlation between relaxation frequency and nanofiller size or filler conductivity is not experimentally available at this stage, this study along with the previous ones indicate that the relaxation frequency could be pushed to higher values or made broader by controlling the filler dispersion in the nanocomposite, making the conducting particles finer and preventing charge leakage by an insulating layer coating (Fig. 15).

Moderate dielectric loss is known to be advantageous for decoupling. Numerical analysis of several embedded distributed capacitance power planes shows that the dielectric impedance oscillates with lower magnitude when the loss of the dielectric is higher [12]. The resonant frequency depends on the length of the resonator and the square root of the dielectric constant. By increasing the loss tangent, the resonant oscillations are suppressed considerably which results in relatively flat impedance over the broad frequency range. Unlike ceramic-polymer nanocomposite films, carbon black-epoxy films can be made much thinner leading to lower inductance. These nanocomposites are hence attractive for power-bus decoupling at intermediate frequencies.

V. CONCLUSION

Nanocomposites with different filler contents of conducting carbon black were characterized for their electrical properties. The composites showed strong relaxation behavior at low frequencies, as predicted in the previous studies. However, the film retained up to 10 times higher dielectric constant than the base polymer, even at 4–5 GHz frequencies, indicating that these composites can be good candidates to replace ceramic-polymer composites. Further improvements in the dielectric constant can be achieved with fillers of higher conductivity and an insulated coating around the nanofiller to prevent leakage. Thicker films showed higher dielectric constant than thinner films. Owing to the nanofiller particles (20–30 nm), the films can be thinned down to 2 μm without any loss in the yield, which is difficult to achieve with ceramic-polymer composites.

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