Tailoring the Temperature Coefficient of Capacitance (TCC), Dielectric Loss and Capacitance Density with Ceramic-Polymer Nanocomposites for RF Applications

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Abstract

High-*k* inorganic materials generally show high loss or high TCC or both, making them unsuitable for RF capacitor applications where high Q, tolerance and thermal stability are critical. Most polymers do not have the required total set of attributes, making it extremely challenging to integrate high-performance RF thin film capacitors in organic packages and boards. In this paper, we demonstrate a strategy to tailor the properties of polymeric composite materials and satisfy all the RF capacitor requirements. With this strategy, it is feasible to meet low TCC and low loss while increasing the capacitance density or permittivity to miniaturize RF components.

Introduction

Embedding of passive components (capacitor, resistor, inductors etc.) onto organic boards is becoming an important strategy towards miniaturization and cost reduction of RF modules [1-2]. Among RF passives, ceramic-polymer-nanocomposites have been explored for embedded-capacitor applications for more than a decade [3-11]. However, all the research focused on decoupling applications for low-frequency I/O circuits/bypass-capacitors, where the quality-factor, temperature-coefficient-of-capacitance (TCC) is not of much concern. Recently, there is increasing trend towards miniaturization of integrated wireless products where several RF components are needed to meet the impedance and signal matching requirements. Some RF designs dictate that the loss has to be <0.005 to meet the performance. The range of capacitance values depends on the applications and varies from few pF up to even 100s of pF. For many applications, the capacitance value has to be stable within 0.2 % over 100^{o}C range of temperature. Several solutions exist and are already patented for thermally stable RF LTCC capacitors because glass has thermally stable properties and low-loss. However, for the emerging organic RF packaging application there is limited availability of organic compatible high-dielectric constant (*k*) and low-loss materials that have good thermal stability. The best solution for a miniaturized-RF capacitor is a polymer-ceramic-nanocomposite, where the polymer enables low-temperature large-area processing while the ceramic-filler increases the *k* of the nanocomposite. Nanocomposite research to date is based on epoxies and ferroelectrics like $BaTiO_3$ (BT) which has very high TCC and loss. Epoxy-BT composites cannot achieve loss <0.01 or TCC within 100ppm/C. Ferroelectrics like BT generally has high-loss (>0.01) and are not easily suited for RF applications. Most ceramic fillers are made from low-temperature synthesis methods leading to further increase in loss (>0.03). Therefore, none of the current BT-epoxy nanocomposites know-how is suitable for high performance RF-capacitor requirements. Novel composite formulation with low-loss polymer matrix-composites is essential to develop capacitors for low-cost RF applications.

In this paper we present two approaches for controlling the magnitude and the sign of the TCC as well as increasing its *k*. The processes include (i) combining polymer-matrix and nano-ceramic-fillers, whose TCCs have different signs to each other (ceramic-polymer nanocomposite, CPN) and (ii) chosing two-kinds of nano-ceramic fillers (ceramic-ceramic-polymer nanocomposite, CCPN) with negative and positive TCC in polymer-matrix thus making the net TCC of nanocomposite close to zero as well as increasing *k*. In CPN capacitor, depending on the temperature range and the filler materials used, the capacitor can be designed to have a low or desired TCC. In CCPN capacitor, the increased capacitance of the positive TCC fillers with increasing temperature is compensated by the decreased capacitance of negative TCC fillers with increasing temperature. Fig.1 shows the basic concept to achieve low TCC in CCPN capacitor.

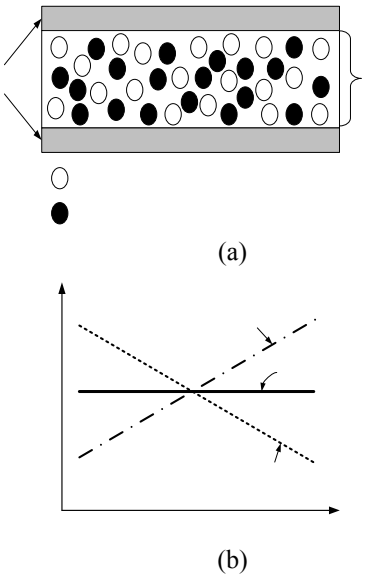

Fig. 1 (a) Schematic of nanocomposite capacitor made of positive and negative TCC fillers and (b) its TCC behavior to be expected.

With the CCPN approach, it is possible to choose the filler loading and achieve higher dielectric constant. In addition,

polymer matrix provides an ideal platform for varying the packing density, which affects the dielectric properties of capacitor. The packing density can be easily increased by a bimodal distribution of these two filler particles where the finer particles fill the interstitial empty spaces (porosity) between the coarser particles.

Experimental

In the ceramic-polymer nanocomposite fabrication, barium titanate (BT) was selected as filler (BT-8, Cabot Inc., PA, particle size ~200 nm). BT, being well-known ferroelectric material, has a high dielectric constant around 6000 at a fine grain size of ~1μm, and of 1500-2000 at a coarse grain size [12-13]. It has both positive and negative TCC regions between room temperature and its curie temperature (~130^{o}C) [12-14]. The BT powders were suspended in dispersant (BYK W9010, Byk-Chemie USA, Wallingford, CT) and PGMEA as solvent (Aldrich chemical company, Inc., Milwaukee, WI). The suspensions were then milled for overnight. BCB (Cyclotene 4026-46, from Dow Chemical Company, Midland, MI) was selected as the polymer matrix. It has been used as a dielectric material for wafer-level packaging applications because of its low dielectric constant (2.65), a low loss tangent (between 0.0008 and 0.002), low moisture absorption, systems [15]. Based on our preliminary measurements BCB has negative TCC. BT-BCB nanocomposites with different ceramic filler loading (14%, 30% and 50%) were formulated by adding each different amount of BCB to the suspensions. After milling them for couple of hours, the mixed slurry was spin-coated on a copper-clad high T_g FR-4 laminates at 3000 rpm for 30 seconds. The samples were then cured in conventional oven under nitrogen atmosphere according to the curing profiles recommended for BCB materials (soft curing for 40 min at 210^{o}C and hard curing for 1 h at 250^{o}C). The final thickness of nanocomposite materials was found to be <10 μm. Finally, 1 μm thick copper top electrodes were deposited by sputtering through a shadow mask.

Results and Discussion

The scanning electron micrograph of the nanocomposite film morphology for 50 vol% filler loading is shown in Fig. 2. From the figure it is clear that the ceramic and polymer dispersion is uniform with little or no agglomeration which indicates compatibility between the BCB and the BT particles with dispersant.

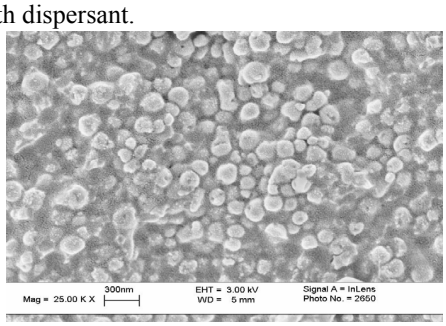

Fig. 2 SEM micrograph of BT-BCB nanocomposite with 50 vol% ceramic filler loading.

The dielectric properties of BT-BCB nanocomposite as a function of filler loading at room temperature is depicted in Fig. 3. From the figure, it is clear that the dielectric constant of the nanocomposite increases with filler loading. The maximum dielectric constant of 33.73 was noticed for the nanocomposite with 50 vol% ceramic filler loading at 100 kHz. Dielectric loss was very low (0.007) at the filler content of 14 vol%, and increased with ceramic filler loading and becomes independent of the amount of The dielectric loss of BT-BCB nanocomposite with higher filler loading is not as low as anticipated, even if BCB as the polymer matrix and it is in well agreement with earlier report in metal and BCB polymer nanocomposites [16]. For higher filler loadings, because of the higher ceramic filler the losses are much higher than that of the BCB polymer, almost approaching that of BT. In addition, the losses from the matrix itself tend to increase because of distortion in the polymer structure interfacing with ceramic particles. However, these values are still much lower than the widely reported BT-epoxy nanocomposites with the same ceramic filler loading (~0.025) [11].

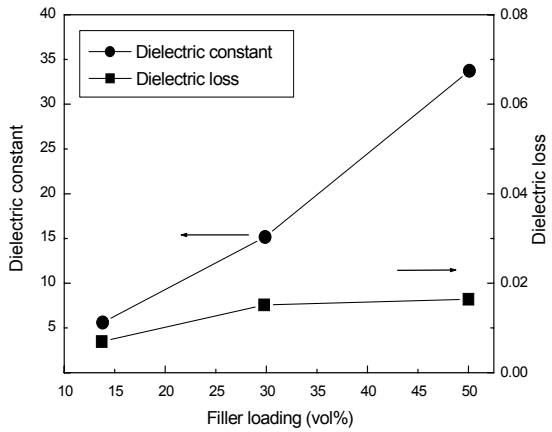

Fig. 3 Room temperature dielectric properties of BT-BCB nanocomposites (at 100 KHz) with ceramic filler loading.

The variation of nanocomposite dielectric constants with temperature is shown in Fig. 4. For the lowest ceramic filler loading (14 vol%), the dielectric constant decreases with increasing temperature over the whole temperature range of measurements and the nanocomposite showed negative TCC over the whole temperature range. With increasing ceramic filler loading (30 vol%), the dielectric constant still decreases with increasing temperature, but becomes stable at higher temperature (above 110^{o}C). With the highest ceramic filler loading (50 vol %), the dielectric constant decreases initially with increasing temperature, similar to those of lower ceramic filler loading, but more abruptly. However, with further increase in the temperature, the dielectric constant rather increases. The nanocomposite with 50 vol% ceramic filler loading showed both negative and positive TCCs depending on the temperature.

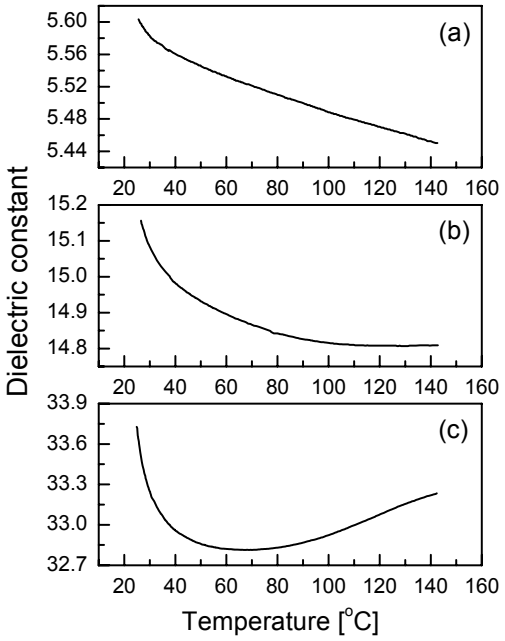

Fig. 4 Temperature dependence of the dielectric constant of nanocomposites with different ceramic filler loading: (a) 14 vol% (b) 30 vol% and (c) 50 vol%.

In order to examine the TCC behavior of nanocomposites with ceramic filler loading, their dielectric constants were normalized with respect to their values at room temperature (Fig. 5). The normalized dielectric constant of pure BCB with temperature is also shown in Fig. 5. BCB has negative TCC over the whole temperature. It is well-known that the dielectric constant of ceramic powders depends on the particle size [14, 17] and grain size, and is very different from the values obtained for bulk samples. Direct measurement of powder dielectric constant is not feasible for fine powders. The dielectric constant can be, however, back-calculated from theoretical models that predict the effective dielectric constant of a two-phased nanocomposite. In this study, dielectric constants of BT powder for different temperatures were calculated with modified Lichtenecker's law using the dielectric constants measured for the nanocomposite and BCB [18]. The modified Lichtenecker's law, commonly used to predict the effective dielectric constant of ceramic-polymer 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 ε_c, ε_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. It is typically 0.3 for well dispersed ceramic-polymer composites [19]. Eq. (1) is arranged as follows:

$$\frac{(\log \varepsilon_c - \log \varepsilon_m)}{(1-k)} = \log\left(\frac{\varepsilon_f}{\varepsilon_m}\right) v_f \qquad (2)$$

Then ε_f can be calculated from the slope (log ($\varepsilon_f/\varepsilon_m$)) of the linear fit between (log ε_c-log ε_m)/(1-k) and v_f. The calculated dielectric constant of BT powders for the whole temperature range are normalized and plotted in Fig. 5. BT has both negative and positive TCC region depending on the temperature. The temperature dependence of dielectric constant for BT is similar to that reported in the literature [12-14].

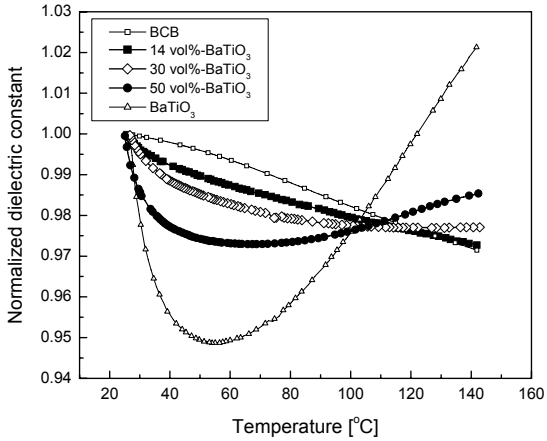

Fig. 5 Normalized dielectric constants of nanocomposites with different ceramic filler loading, pure BT and pure BCB as a function of temperature.

Fig. 5 shows clearly that the TCC of nanocomposite can be changed by adjusting the volume fraction of its two constituents with different TCC behavior. Table 1 lists the TCCs of nanocomposite, pure BT and pure BCB depending on temperature region, which are calculated from either Fig. 3 or Fig. 4. At lower temperatures (25<T<55°C), the TCCs of BT and BCB reinforce each other, leading to a more negative TCC with increasing ceramic filler loading. Nanocomposite with 50 vol% ceramic filler loading has the highest negative TCC leading to an abrupt decrease in dielectric constant of nanocomposite with temperature, as shown in Fig. 4(c). All the nanocomposites have more negative TCC than pure BCB matrix but lower than pure BT. In the positive TCC region of BT (> 55°C), the decreased dielectric constant of BCB with temperature is compensated by the increased dielectric constants of BT with temperature. At 14 vol% ceramic filler loading, the nanocomposite's TCC is still negative but lower than pure BCB. This demonstrates that there is a compensation effect between the positive TCC of BT and negative TCC of BCB even at the low ceramic filler loading. At 30 vol% ceramic filler loading, the nanocomposite has more compensation effect than that of 14 vol% ceramic filler loading, which results in lower negative TCC. Especially above 110°C, near zero TCC can be achieved (0.29 ppm/°C). By further increasing ceramic filler loading to 50 vol%, BT plays a dominant role in the nanocomposite behavior and therefore the nanocomposite has positive TCC, but still lower

than that of pure BT because it is partially compensated by BCB.

Table 1 TCCs of nanocomposites, pure BT and BCB

Tempe-rature (°C)	Nanocomposites' TCC (ppm/°C)			BT TCC (ppm/°C)	BCB TCC (ppm/°C)
	14 vol%	30 vol%	50 vol%		
25 ~ 55	-812	-1,361	-2,624	-5,980	-160
>55	-200	-180	231	1,132	-270

Curie temperature was not distinctly observed around 120-130 °C either in our BT-BCB nanocomposite measurements or from the calculated dielectric constant for pure BT powder. The Curie temperature corresponds to the transformation of crystal structure from a distorted tetragonal to a normal cubic perovskite. X-ray diffraction (XRD) was performed to investigate the crystal structure of BT powder used in this study. Figure 6 shows the {220} reflections obtained from the BT powder. While clear splitting of {220} reflection that distinguishes tetragonal from cubic phase was not observed [11, 14], some weak splitting of the peak was observed as shown in the magnified view of XRD pattern. It is thought that the BT particles still retain a little portion of tetragonality though most of the BT has cubic structure. Considering the small particle size of our BT (<200 nm), its weaker tetragonality is in accord with the fact that tetragonality decreases with decreasing particle size [14, 20]. Because of the loss in tetragonality at finer particle sizes, distinct Curie temperature was not observed.

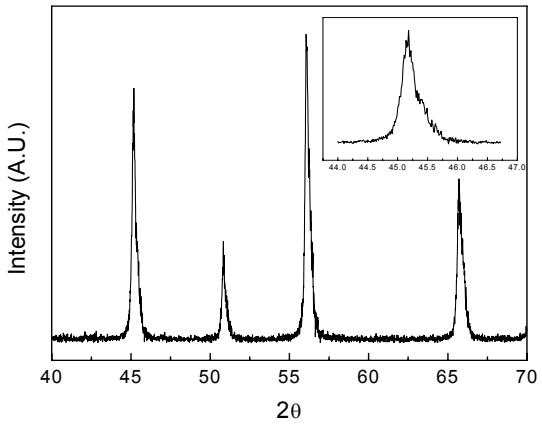

Fig. 6 {220} reflections from XRD patterns of BT powder used in this study.

High frequency properties

Low inductance and low loss are essential for good performance for RF capacitors. Low inductance increases the resonance frequency; hence the capacitor can be applied at higher frequencies. Low loss results in high Q capacitors. In addition to this, a stable dielectric constant with respect to frequency is also necessary. The high-frequency measurements were taken using a vector network analyzer (VNA), and air coplanar probes. Figure 7 shows the magnitude of the impedance for a capacitor having an area of 1.095 cm^2 and a thickness of 10 μm. The high resonance frequency of around 800MHz is due to the low inductance, which was measured as 27pH. Figure 8 shows that the capacitance is fairly constant with respect to frequency up to about 1.4GHz.

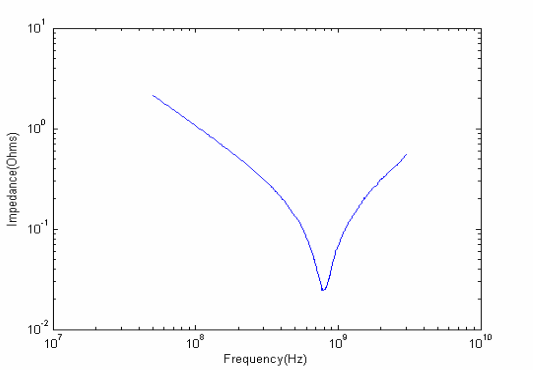

Fig.7 Magnitude of the impedance vs. frequency for a capacitor with an area of 1.095 cm^2 and thickness of 10 μm.

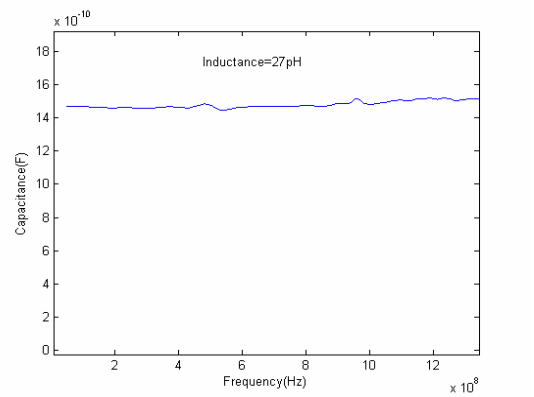

Fig. 8 Capacitance vs. frequency for a capacitor with an area of 1.095 cm^2 and thickness of 10 μm. The dielectric constant of the material is ~17.

Conclusions

Here we report, our first attempt, to control the sign and magnitude of the TCC of nanocomposite dielectric for embedded RF capacitors. The TCC of the nanocomposite was significantly influenced by the TCCs of its constituents (polymer matrix and ceramic filler) and could be tailored by combining a positive TCC material with a negative TCC material. In our BT-BCB nanocomposite, the positive TCC of BT ceramic filler was compensated by the negative TCC of BCB polymer matrix, leading to positive-zero-negative TCC values by adjusting the volume fraction of the ceramic filler or polymer matrix. With nanocomposite dielectric materials, depending on the fillers or matrices used, the capacitor can be easily designed to have a low or desired TCC.

Acknowledgments

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