Solution Processed High Capacitance Nanocomposite Dielectric for Printed Electronics Applications

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Abstract
Since early last decade, scientists had succeeded in applying printing-related technologies to create organic field effect transistors (OFETs) with micron-sized features. This has led to a wide- spread vision of developing printed electronic products, especially sensors, displays, and low cost wireless products such as radio frequency identification tags (RFIDs). The market opportunities for many of these applications depend strongly on materials and manufacturing cost. Towards this end, we have developed a ferroelectric/epoxy nanocomposite dielectric, whose advantages in terms of processability, low processing temperature, low cost, and versatility make it quite promising for printed electronic applications. In this paper we present our work to develop low cost printed capacitors with five micron thick nanocomposite dielectric with a high capacitance density of about 62 pF/sq. mm. with low dielectric loss (approximately 3%) and quite low current leakage.

Solution processed, high capacitance nanocomposite dielectric material was demonstrated as a low cost insulating material for printed electronics applications. A nanocomposite dielectric consisting of cross-linked propylene glycol methyl ether acetate and barium titanate (BTO) nanoparticles was developed and utilized as a printed dielectric. The high relative permittivity (K=35), bimodal nanocomposite system utilized has two different filler particle sizes 200 nm. and 1000 nm. diameter particles. Due to the nanosize of the BTO particles, they disperse well in the organic matrix, which makes it possible to use solution-processable methods, such as pad printing.

Introduction

The primary goal of printing electronics is to create structures that are functionally similar to conventional electronics but at a far greater production speed, lower cost, and with less manufacturing complexity [1]. A wide variety of conventional and new printing technologies are being used or tested for printing electronic circuits of various types. However, the varied nature of the materials available to create such circuits and the diversity of circuits required means that no one printing technology will ever be used for all applications. Indeed, the evolution of new conducting, semiconducting, dielectric, battery and other inks with new physical characteristics means that the printing technologies chosen or adapted will be constantly changing for some time to come. To make the transition towards materials that are printed in ambient conditions (as opposite to highly–controlled environment) it becomes necessary to use either a suspension or solution of material (ink), which can be layered to approximate the bulk properties of a solid formed by a traditional deposition process[2].

Ceramic-polymer composite dielectrics are promising candidates for printed electronic applications where low processing temperature is essential. Barium titanate (BaTiO3) is an ideal dielectric due to its high dielectric constant, and is available in a wide range of particle sizes at commodity prices. However, BTO is not solution processable which limits its application in low cost printed electronics. Epoxy resin is an ideal polymer matrix due to it low processing temperature, and a curing reaction that is initiated by a thermal agent or photosensitizer. Epoxies are also known for their stability with respect to frequency at normal temperature ranges [3]. Incorporating barium titanate particles into the epoxy matrix, results in the creating of a solution-processed composite with high dielectric constant. This approach combines the low-temperature ($<200\,^{\circ}C$) processing of the organic epoxy matrix and the high dielectric constant of the ceramic BTO filler.

A number of ceramic-polymer composites developed to date are microcomposites with the dispersant particle size ranging from a few to ten microns [4]. Due to their large particles size, precursor solutions of microcomposites face limitations in processing them into thin films or as printed inks in direct write or screen printing processes which are essential fabrication techniques for printed electronics. This problem can be overcome by employing nanoparticles of BTO as long as no significant particle agglomeration takes place.

Printed capacitors were developed using a combination of pad printing and coating technologies. An aluminum coated Mylar film was used as the flexible bottom electrode substrate. The BTO/Epoxy nanocomposite was printed and thermally cured before a silver top electrode was pad printed to complete the capacitor structure. The low temperature processing of the BTO nanocomposite dielectric is compatible with the flexible substrate used without compromising performance or reliability. In this paper we present our work to characterize and process the nanocomposite. Electrical characterization of printed thin film capacitors is also described.

Material Characterization

A specialty bimodal nanocomposite was formulated by an electronics materials supplier for our evaluation. A two-part epoxy consisting of propylene glycol methyl ether acetate was utilized as the polymer matrix. The barium titanate ceramic filler consisted of two different particle sizes: 200 nm. and 1000 nm. diameter at a particle distribution ratio of 1:3 by weight. Having two different particle sizes enhances the BTO particle surface coverage in the cured film and results in a higher nanocomposite dissipation factor. The nanocomposite had a 60v% particle loading. Increasing the volume fraction of the filler beyond 0.5-0.6 is a formidable task and compromises have to be made on the mechanical properties and the processability of the nanocomposite [5]. The BTO particle surface coverage was quite uniform as can be seen from the scanning electron microscopy (SEM) image of the cured dielectric shown in Figure 1. The dielectric curing process is partially responsible for the particle agglomeration seen in the SEM image.

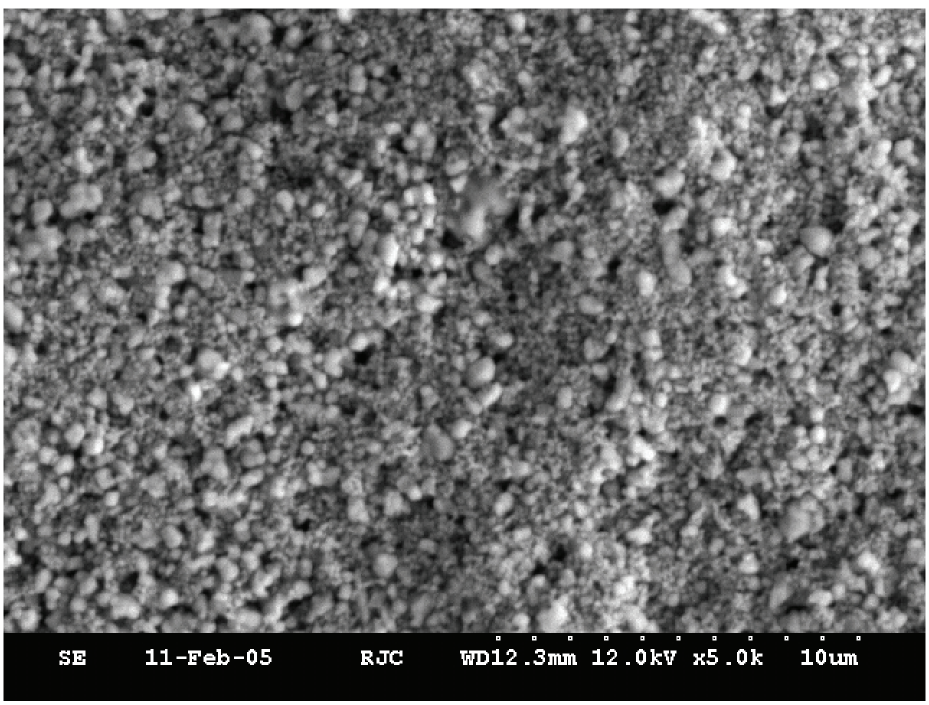

Figure 2 - SEM image of BTO Nanoparticles in the Cured Dielectric

Curing behavior of the nanocomposite was investigated using a differential scanning calorimeter (DSC, Model 2200 from TA Instruments). After curing, the glass transition temperature (Tg) was measured using DSC under modulated mode. The curing profile with the 60v% filler is shown in Figure 2. The cure reaction stars at about 65 $^\circ C$ and the curing peak appeared at approximately 85 $^\circ C$. The Tg of the nanocomposite is around 70 $^\circ C$. To ensure complete curing, the nanocomposite was cured at 150 $^\circ C$ for 1 hour in a ventilated oven. The curing behavior displayed makes the nanocomposite suitable as a printed insulator on flexible organic substrates.

BTO/Epoxy nancomposite viscosity is a critical factor in processing printed capacitors. Viscosity was determined using a CVO 120 high resolution rheometer from Bohlin Instruments. Testing of the nanocomposite immediately after mixing the two parts (epoxy resin and hardener) showed a low viscosity of only 1.21 Pas. Processing the nanocomposite dielectric with this low viscosity will be very challenging. Having a higher viscosity dielectric will lend itself better to the type of low cost pad printing or coating targeted for printed electronic applications.

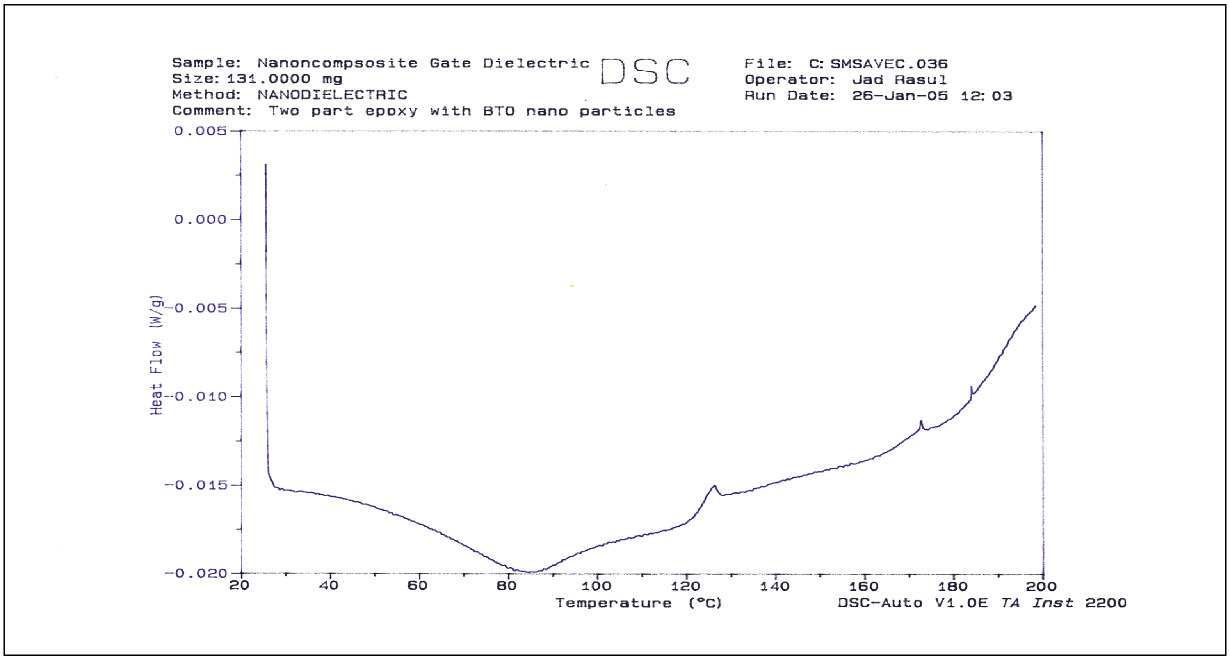

Figure 2 - Curing Profile of the BTO/Epoxy Nanocomposite

Previous investigation of the pad printing process indicted that optimum printing can be achieved with viscosities higher than 3.0 Pas. Drying the nanocomposite at room temperature will result in the solvent evaporation that ultimately leads to higher viscosity. Figure 3 shows the viscosity and shear properties of the nanocomposite dielectric 20 hours after mixing. With a Newtonian model fit, the viscosity was determined to be 3.04 Pas. This viscosity is more compatible with the low cost pad printing process that was utilized for capacitor fabrication.

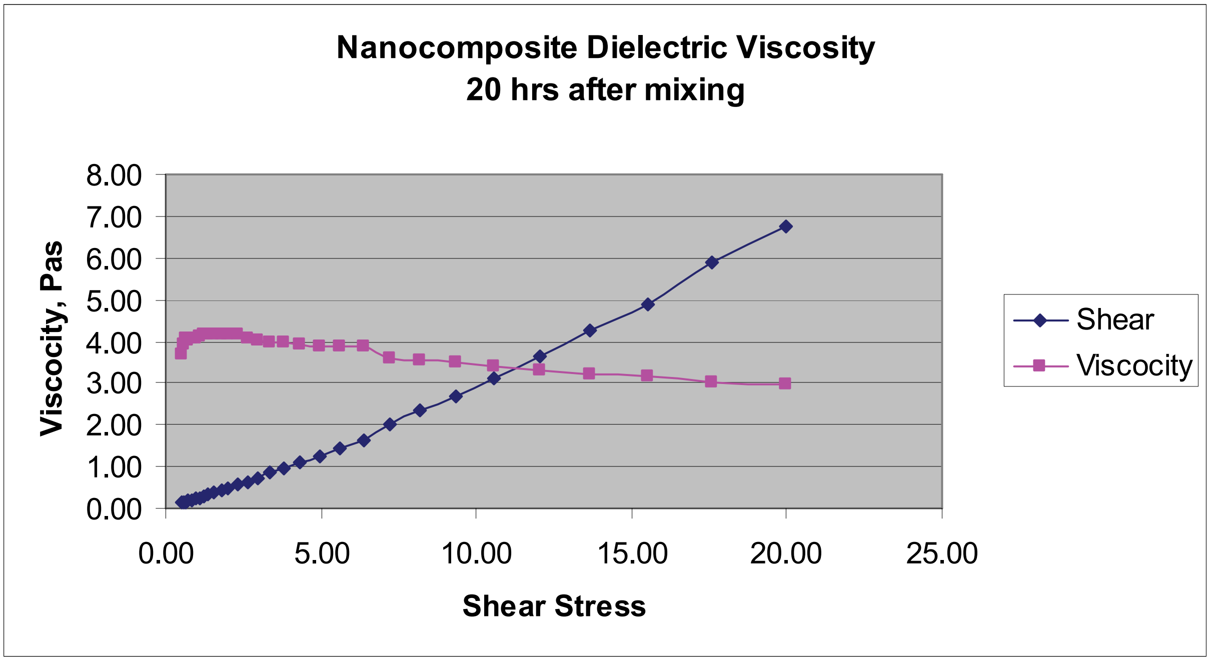

Figure 3 - Nanocomposite Dielectric Viscosity 20 hours After Mixing

Capacitor Printing

Electrical characterization of the nanocomposite dielectric was done through the fabrication of parallel plate capacitors. Fabrication of the nanocomposite capacitors was achieved utilizing the low cost pad printing process. The pad printing process is a material transfer process that is commonly used in printing inks on flexible and curved surfaces such as printing logos on mugs and fabrics. Utilizing the pad printing process for printing electronic circuits represents a challenge due to processing and materials issues. However, pad printing is a good candidate for high volume, low cost plastic electronic applications. In the consumer electronics area, a possible route is the development of production processes that could combine low manufacturing cost with the ability to produce short runs of products with different configurations and features. Pad printing utilization could also result in reductions in the size and cost of many electronic products and allow designers to add electronics in other ways, such as in fabrics or product packaging. Possible applications include printing electronic circuitry onto substrates, including curved shapes, to add functions to an object without adding materially to its weight or volume.

The ink transfer process in pad printing is commonly referred to as *offset gravure* because the ink is held in an etched surface which is brought in contact with a carrier offset surface (the pad) that subsequently transfers the image to the substrate [6]. A Trans Tech SEALCUP 60, all-mechanical, cam-operated bench model pad printing machine with a hermetically sealed ink cup was used to print the BTO nanocomposite dielectric as well as the top silver electrode layer. An aluminum coated Mylar film was used as the flexible bottom electrode substrate. The capacitor fabrication process is shown in Figure 4. The nanocomposite dielectric was pad printed onto the aluminum coated Mylar film at ambient conditions. The pad printing program consisted of a 2 second dip of the cup in the material reservoir followed by a 5 second dwell time where the cup was exposed to air. The final step consisted of the cup making contact for 2 seconds with the aluminum coated Mylar film that was vacuum held onto the workstation. The square shaped dielectric was transferred to the aluminum coated film. To insure a pinhole free surface, the 1 hour dry oven curing at $150\,^{\circ}C$ was preceded by a 1 hour flash-off at ambient conditions. The final step in the capacitor fabrication process involves pad printing the top silver electrode. Silver paste from Dupont (5028 Silver Conductor Paste) was pad printed using the same set up as before. Curing was done in a dry oven for 20 minutes at $120\,^{\circ}C$. As such, square-shaped, parallel plate capacitors have been fabricated. The fabricated capacitors had a 5 um. dielectric thickness as measured using an optical profilometer.

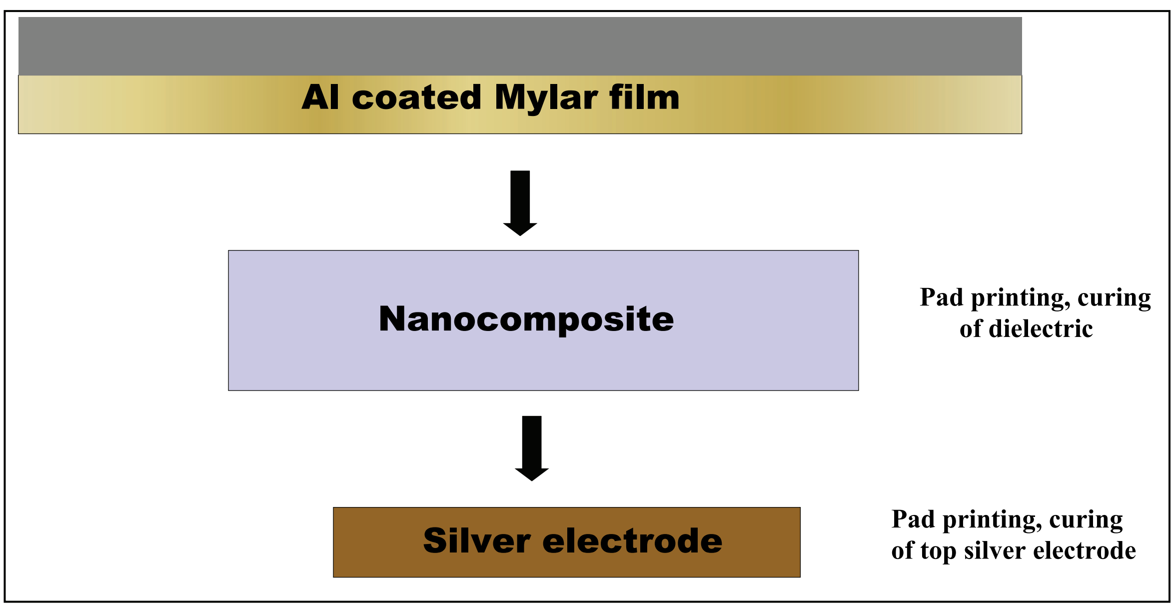

Figure 4 - Fabrication Process of Capacitor Prototype

Electrical Characterization

Capacitance measurements were taken using an HP 8753C Network Analyzer from 30 KHz to 1000 MHz., and is shown in Figure 5. Capacitance density was determined to be 62 pF/sq.mm. with a loss tangent of 3.2% at 30 KHz. Dielectric constant value was calculated from the capacitance data using Equation 1.

$$C = \frac{\varepsilon_0 \varepsilon_r A}{t} \qquad \text{Eq. 1}$$

where, ε_0 is dielectric constant of the free space (8.85 x 10^{-12} farad/m), A is the area of the electrical conductor plate, t is the thickness of the insulating layer, and ε_r is the dielectric constant of the insulator layer. The nanocomposite dielectric constant was calculated to be 34.9.

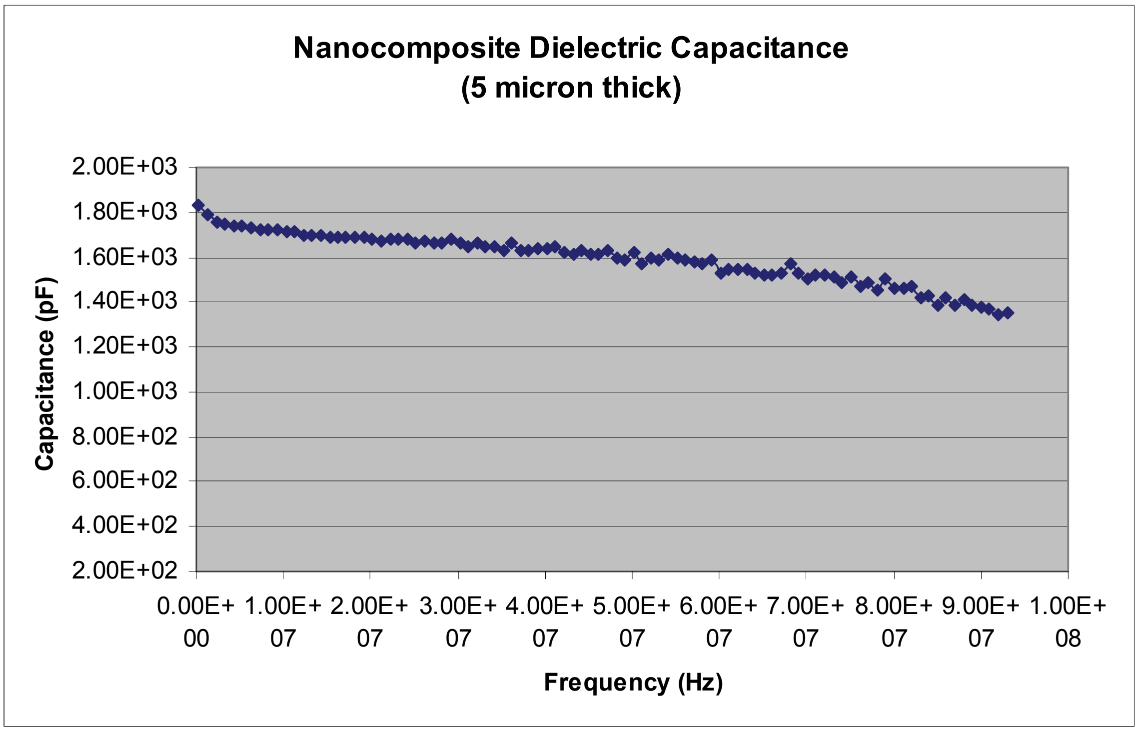

Figure 5 -Nanocomposite Dielectric Capacitance as a Function of Frequency

Conclusion

We have developed a promising low temperature, low cost approach to process high capacitance BTO/epoxy nanocomposite dielectric thin films for printed electronics applications. It has been demonstrated that the pad printing technology can be utilized to process thin films insulators of the nanocomposite. Thermal and electrical properties of the nanocomposite dielectric films have also been characterized. The high capacitance density obtained suggests that the BTO/epoxy nanocomposite can be utilized to reduce the operating voltage of printed electronic devices.

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