White Paper: Transparent High Dielectric Nanocomposite

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Abstract

High dielectric constant materials have a wide array of applications. Most high dielectric constant materials are inorganic, which are typically difficult to process. Polymer materials are gaining popularity due to their processability and flexibility. They, however, has relatively low dielectric constant. Pixelligent's transparent ZrO2 nanocrystal/polymer nanocomposite provides a new class of high dielectric constant material that can be applied to many novel applications. Because of our proprietary surface capping technology, the nanocrystals can be incorporated into the polymer up to 80 wt% loading, corresponding to a dielectric constant of 8, without losing optical transparency and processability.

Background on Dielectric Materials

Dielectric materials have very broad applications in the electronic industry, including capacitors, gate dielectrics for transistors, and electrostatic dissipation (ESD) coatings. A non-magnetic dielectric material is defined by real and imaginary components of the Complex Permittivity:

$$\epsilon^* = \epsilon' - j\epsilon'' \; [F/m]$$

Normalization of ε^* with respect to the Dielectric Permittivity of Free Space $\varepsilon_o = 10^{-9}/36\pi$ [f/m] gives the Complex Relative Permittivity:

$$\frac{\epsilon^*}{\epsilon_0} = k^* = k' - jk''$$

k' and k" indicate capability of storage of electric field energy and dissipative characteristics for non-magnetic dielectrics. Dielectric Constant k' is the relative permittivity or dielectric constant. It is the quantity generally referred to as Dielectric Constant in the literature. It is a dimensionless quantity since it is relative to free space. Dissipation Factor (D), also called Loss Tangent or tan δ, is usually reported to indicate the energy loss characteristic of a material. It is also dimensionless and is defined as follows:

$$D = tan\delta = k''/k'$$

Lossy dielectrics are characterized by a dissipation factor greater than 0.1. They may or may not exhibit DC electrical conductivity. Dielectric properties usually vary with frequency; in general, the higher the DC conductivity, the greater the frequency sensitivity. Dielectrics with a dissipation factor less than 0.01 are considered low-loss materials and good electrical insulators. In general, dielectric properties show relatively little variation with frequency in the microwave range.

Table 1 shows the dielectric constant and dissipation factor for common dielectric materials. Various combinations of dielectric constant and dissipation factor are used in different applications. For example, a high dielectric constant and a low dissipation factor are desired for gate oxide integrated circuit applications. A high dielectric constant and a high dissipation factor are desired for ESD coatings.

Table 1 illustrates that most high dielectric constant materials are inorganic materials. As a result dielectric materials are traditionally made from inorganic substances. However, these materials are difficult to process, usually requiring high temperature process conditions, and are brittle and inflexible. Polymers are gaining wider use as dielectric materials for many applications such as flexible and printable electronics. This is due to increased processability, greater flexibility, and improved chemical resistance. . However, most polymers have a dielectric constant between 1 and 4 [1], severely limiting their use in many applications.

Table 1: Properties of common materials [1] (The green cells indicate polymeric materials. The blue area indicates the range of properties that can be developed from Pixelligent's nanocomposites).

Dielectric Constant \ Dissipation Factor	0.0001	0.0002	0.0003	0.0004	0.0005	0.0006	0.0007	0.0008	0.0009	0.001	0.002	0.005	0.01	0.05	0.1	1
1																
2																
2.1	Teflon™										Natural Rubber					
2.2																
2.3	Poly-ethlylene										Fluro-polymer					
2.4																
2.5		Poly-styrene										Lexan™	Nitirle Rubber			
3		Fused Silica									Mylar™		Epoxy Silicone	PMMA	Zinc Oxide	
4			Boron Nitride							Borosilicate Glass		Pyrex™				
5			Mica													
6				Berrylium Oxide									Soda lime Glass		Molybdenum Sulfide	
7																
8																
9			Sapphire	Magnesium Oxide		Aluminum Oxide										
10											Magnisium Titante					
15																
20														Zirconia		
50											Titanium Dioxide					
100																
>100											Strontium Titante				Barium Titanate	

Dissipation Factor

Pixelligent's High-Dielectric Constant Nanocomposites

Nanocomposites composed of inorganic nanocrystals and polymer matrices offer a greater range of dielectric properties without sacrificing other properties of the polymer. Nanocomposites are a rapidly developing family of materials. They have a wide array of applications. A nanocomposite is a synthetic material composed of one or more types of nanocrystals (i.e. fillers), usually embedded in a polymeric binder. A nanocomposite is an effective way to combine the advantages of the constitute materials.

Nanocrystals are particles of a material, typically tens of nanometers or smaller, that retain the stoichiometry and crystal structure of their bulk counterpart. Nanocrystals have been the focus of accelerated scientific studies for the past two decades because they often demonstrate novel properties as a result of the reduced sizes. Moreover, nanocrystals can be surface treated with various capping agents and dispersed into polymer matrices to form nanocomposites that can be used in applications where bulk materials are impractical or when novel and integrated functionalities are required. When nanocrystals are dispersed into an optically transparent polymer, the dielectric constant of the resulting nanocomposite can be described using effective medium theory, for example, Maxwell Garnett theory: [2]

$$\frac{\varepsilon_{eff} - \varepsilon_m}{\varepsilon_{eff} + 2\varepsilon_m} = \delta_i \left(\frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i + 2\varepsilon_m} \right)$$

where ε_{eff} is the effective dielectric constant of the medium, ε_i is the one of the inclusions and ε_m is the one of the matrix δ_i is the volume fraction of the nano-filler.

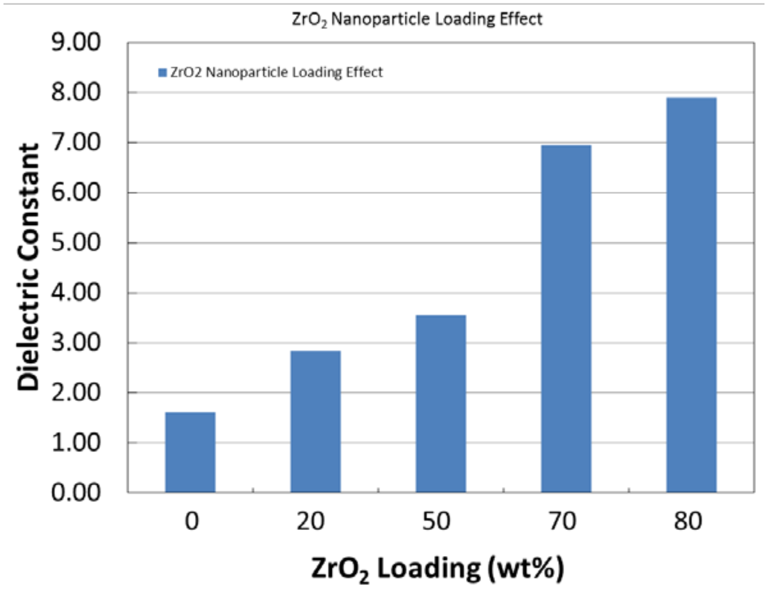
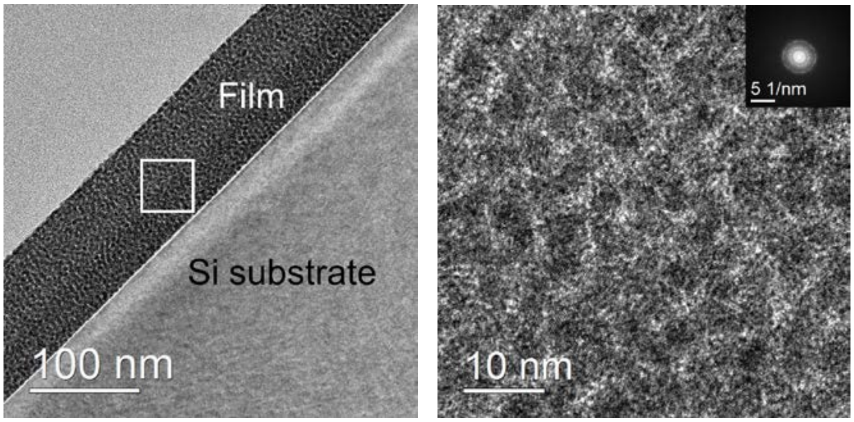


Figure 1. Dielectric constant of the ZrO_2/Acrylic Nanocomposites with different loadings. For reference, silicon dioxide, a commonly used dielectric material for gate oxide, has a dielectric constant of 3.9.

The small (< 10 nm) and uniform size of Pixelligent's nanocrystals, and our proprietary surface modification technology ensure that when the nanocrystals are loaded into a polymer matrix, they are entirely agglomeration free with superb homogeneity. The quality of the nanocomposite and film is demonstrated in Figure 2.

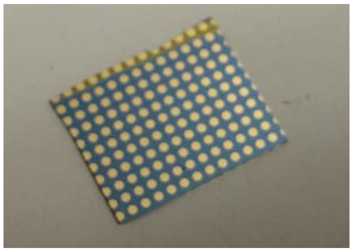
The high quality of Pixelligent's nanocomposite provides low dielectric loss and high optical transparency. To demonstrate the impact of the ZrO_2 nanocrystals inclusion on the dielectric constant, a ZrO_2/acrylic system was used as a model system. The nanocomposite formulation with different ZrO_2 loadings were spin-coated on a conductive silicon wafers, with ~ 2 µm in thickness, then gold electrodes are deposited on top of the film to form a metal-insulator-metal configuration. The capacitance was measured using a LCR meter and the dielectric constant was calculated. The results are shown in Figure 1. Dielectric constant of ~ 8 can be achieved with ~ 80 wt% nanocrystal loading. The measured value is larger than predicted by Maxwell Garnett model, which assumes that there is no interaction between the matrix and filler. Similar results based on ZrO_2 nanocrystals were also observed in the literature, the large dielectric constant was attributed to interfacial polarization as a result of the mixed valency of Zr ions on the nanocrystal surface. [4]



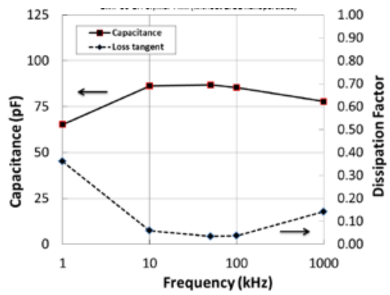
a) b)

Figure 2. TEM images of the nanocomposite films measured. a) shows the uniform film thickness and excellent smoothness; and b) is a high magnification image showing individually dispersed ZrO_2 nanocrystals.

Figure 3a shows the testing structure for the dielectric constant measurements. The films were deposited on a highly conductive silicon substrate, placing gold contacts on top of the film for an array of capacitors. Figure 3b shows a typical capacitance and dissipation factor of a nanocomposite with 80 wt% ZrO_2 nanocrystals. ZrO_2 nanocrystals loading. The dissipation factor of the material is very low even at high frequency. Considering the low thickness of the film, this indicates that the device made with the nanocomposite film will have very low leakage current.



a)



b)

Figure 3. a) Testing structure for the dielectric constant measurements; b) a typical capacitance and dissipation factor of a nanocomposite with 80 wt% ZrO_2 nanocrystals. The dielectric constant can be calculated from the capacitance.

The optical transmittance of these films were also measured, these films are deposited on quartz substrates with similar process conditions. All the films showed good optical transmittance in the entire visible range, as shown in Figure 4.

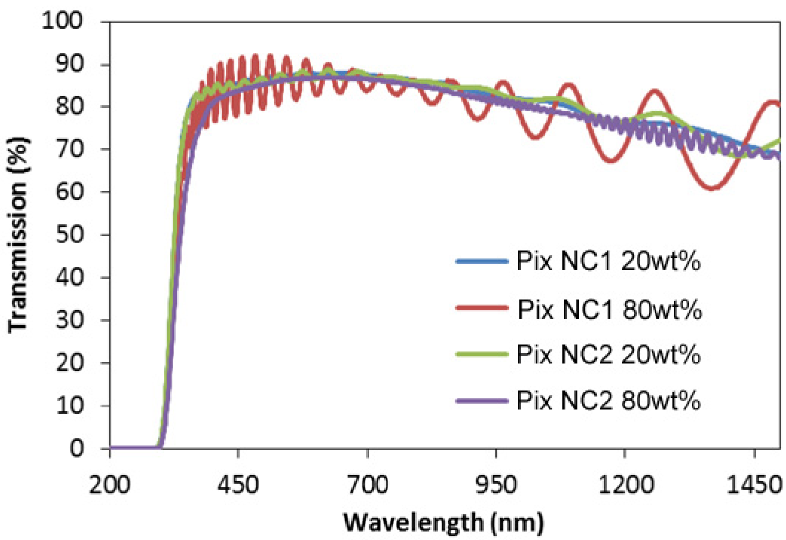


Figure 4. Optical transmittance of two of the Pixelligent's high dielectric nanocomposites. Note: The transmittance were measured without a reference, which means the reflection from the front surface was not taken into account and the actual transmittance is higher than what were shown in the figure.

Pixelligent is capable of dispersing the nanocrystals into a large variety of polymers, such as acrylics, epoxies, silicones, and siloxanes. A similar trend in improving dielectric constant is expected as nanocrystal loading increases in the nanocomposite based on Equation 1.

Pixelligent's ZrO_2 nanocrystal/polymer nanocomposite combines the high dielectric constant of ZrO_2 with the processability of polymeric materials to provide a flexible, and high dielectric nanocomposite that can be easily applied with a thin film coating process such as spin-coating or roll-to-roll printing. Our nanocomposites significantly expand the range of available dielectric constants for polymeric dielectric materials, as illustrated by the blue rectangle in Table 1. Furthermore, Pixelligent's nanocomposites are highly transparent as well as solution processable, allowing them to be used in a broad array of applications such as displays, touch screens, smart windows, optical sensors and printable electronics.

Acknowledgment

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Bibliography

[1] Data cited from Technical Reports AFML-TR-72-39 and 74-250 Laboratory for Insulation Research, Massachusetts Institute of Technology. Measurements are 25°C and 1-10 GHz. Properties vary with frequency and temperature..

[2] H. Nalwa, Handbook of Low and High Dielectric Constant Materials and Their Applications, London: Academic Press, 1999.

[3] T. C. Choy, Effective Medium Theory, Oxford: Clarendon Press, 1999.

[4] S. G. T. &. D. S. K. Manna, "Room temperature stabilized cubic zirconia nanocrystal: a giant dielectric material," *Journal Of Physics D: Applied Physics,* vol. 43, no. 29, p. 295403, 2010.