(Au, Ag)-SiO_2 Core-Shell Nanoparticles Based Polymer Nanodielectrics for Energy Storage Applications

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ABSTRACT

Nanodielectric is an emerging field with applications in capacitors, gate dielectrics, and as energy storage-alternates to Li-Ion batteries such as in communication devices. Nanodielectrics are related to the dielectric phenomenon of nanoscale materials having morphology comprised of nanoparticles, nanowires, nanotubes and nano sheets. Extensive interest is being directed toward research in energy storage solutions for both discrete and embedded capacitors. Since the dielectric behavior can be tailored by simply controlling the type and the amount of the nano-fillers in the host polymer, there is an opportunity to exploit nanocomposites. This paper addresses materials and processes for energy storage in high k embedded capacitors using metal nanoparticles coated and uncoated with SiO_2 shells (M@SiO_2, where M = Au, and Ag,) and high K polymer matrices for stabilization. Specifically, we present the effective fabrication and the properties of Nanodielectrics produced with Ag and Au nanoparticles in a polymer (polyvinyl Pyrroldone, PVP) and Polystyrene (PS) matrices using core-shell nanostructure geometry.

Keywords: Nanodielectrics, nanocomposites, high k polymer, energy storage, capacitors,

1.0 INTRODUCTION

High dielectric constant (k) materials have received tremendous interest recently due to their potential applications in energy storage solutions for electronic equipments [1-3]. In particular, there is a growing demand for capacitors that can store a large amount of charge and deliver it instantaneously [4]. Such storage capacity depends on the type of materials and polarizability of the said dielectric materials. This property is enhanced by adding nanoparticles to the matrix of polymeric material that can greatly improve the thermal, mechanical and electrical properties of the nanocomposites. Further, the electrical properties of nanodielectrics can be improved if the nanoparticles are well dispersed. Since nanoparticles agglomerate easily due to high surface energy and many conventional techniques cannot break-up their agglomerates, making well dispersed discrete nanoparticles in polymer films the key issue to achieving higher performance. Another point of concern is the non-compatibility issue related to nanoparticles and polymer types. Therefore, it is important to explore the possibility of using the intrinsic dielectric property of nanoparticles of silver and gold coated and uncoated SiO_2 shells (M@SiO_2@polymer and (M@polymer; M=Au or Ag; polymer = PVP or PS) films for fabrication of capacitors for energy storage.

1.1 WHY POLYMER CAPACITORS

Nanodielectrics made of metal nanoparticles embedded in a polymer matrix greatly improve the properties of polymer nanocomposites used for energy storage devices. Polymers have high processing ability, mechanical flexibility, electrical breakdown strength and compatibility with several electronic technologies. However, they have a low dielectric constant (k). Embedding metal nanoparticles in a polymer matrix seems to be a very effective way to enhance the dielectric performance of the nanocomposites [5, 6]. The dielectric constant (k) of such nanocomposites increases considerably with increasing metal nanoparticles loading into the host polymer and so does the capacitance of such composites until a specific concentration is reached, after which capacitance drops rapidly. In order to increase the energy storage capability without compromising the inter-particle spacing, we propose to have core-shell capacitors uniformly distributed in the host polymeric films. These improved core-shell embedded devices should allow for storage of a large amount of charge per unit volume that can be released rapidly on demand.

Polyvinyl Pyrroldone (PVP) is extensively used as a dielectric in energy storage capacitors due to its suitability as polymeric matrix for dispersing or embedding nanoparticles with uniform spacing. Its solubility in water and other solvents make it a better candidate for easy fabrication of films. Further, PVP is a potential polymer to act as a protecting agent, reducing agent and nucleating agent in nanoparticles synthesis and it prevents nanoparticles agglomeration. In this paper, we will describe the use of PVP as a polymer matrix for producing high dielectric (k) embedded capacitors using metal nanoparticles both coated and uncoated with SiO_2 shells ($M@SiO_2$, where, M=Au, and Ag).

2.0 EXPERIMENTAL

We are currently exploring a novel combination of spin-coat and PVD methods to produce Nanodielectrics films, which are based on polymer coated noble metal nanoparticles. Nanocomposites made with metallic nano-sphere particles into polymer are a forceful and influential concept for producing high-dielectric constant films with minimum dielectric loss that can be incorporated into the standard capacitor manufacturing process. Core-shell nanoparticles were successfully synthesized through wet chemistry techniques. The following sections enumerate and describe briefly the preparation of silver (Ag) and gold (Au) nanoparticles with and without silica shells dispersed in a PVP polymer film matrix.

Synthesis of Au/Ag-Nanoparticles in PVP

The synthesis of silver colloids was carried out using the procedure as described in literature [7]. 2 ml of 1.16 mM trisodium citrate solution was added drop-wise to a heated (90 degrees) 98 ml aqueous solution of 0.65 mM of silver nitrate while stirring. The mixture was kept heated for 15 min. and then was cooled in ice. To this cold solution, a 1% aqueous solution of PVP was slowly added with constant stirring. The color of the silver nanoparticles in PVP appeared as pale-grey. In a second method, a procedure as described by Chou and Chen [8] was used. Similarly, synthesis of gold-nanoparticles was done using an established [9] using a sodium citrate stabilized method.

Synthesis of Silica-coated Au/Ag-Nanoparticles in PVP

The surface of the gold nanoparticles was coated with uniform silica shells using a procedure developed by Stober and co-workers [10]. According to this method, 10.0 ml of the prepared gold nanoparticles are dispersed into a mixture of ammonia (2.0 ml) and ethanol (20.0 ml). The resulting solution is vigorously stirred for 5 min, after which tetraethylorthosilicate (TEOS, 50.0 uL) is added to initiate growth of the silica shell. The mixture is then stirred overnight at room temperature to result in silica-coated gold nanoparticles. Importantly, the thicknesses of the silica shell can be tuned from 20 nanometers to more than 100 nanometers simply by adjusting the amount of TEOS added to the solution. This allows controlling the metal loading "concentration" in the processed nanocomposites which enhances further the dielectric properties. Silica-coated Ag in PVP nanoparticles were made similarly following the Stober method. Figure 1 illustrates the SEM image of silica coated Au nanoparticles to be used in fabrication of nanodielectric nanocomposites.

Physical Characterization

Physical characterization and surface morphology of the prepared polymer films and nanoparticles were carried out using UV-absorption, SEM/TEM images analysis and I-V characterization.

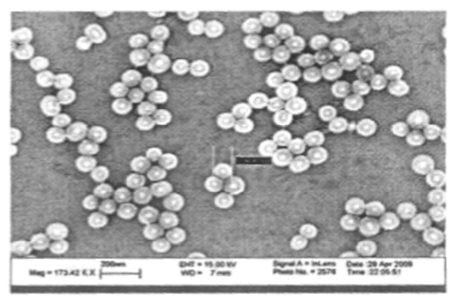
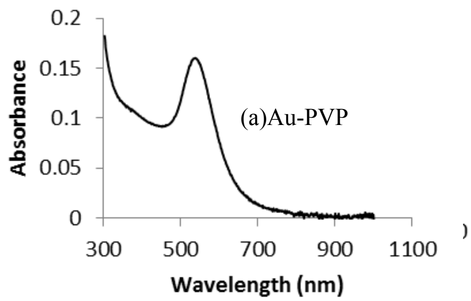


Figure 1: SEM image of $Au\text{-}SiO_2$ composite core/shell nanoparticles

3.0 RESULTS AND DISCUSSION

In order to increase the energy density of polymer composites for capacitors, several important points are to be noted here. Since capacitance depends on film thickness and uniformity of films, these nanoparticles cannot be directly used as a dielectric as they cannot be used as a film coating. Therefore, we proposed to solve this problem by two approaches. First is to load the nanoparticles in a host medium such as PVP polymer and second is to make polymer films embedded with metal-silica (core-shell) nanoparticles. Capacitance of the films coated using nanoparticles or $metal@SiO_2$ core-shells-NPs depend on the amount of PVP, concentration of the NPs and thickness of the films. In the present work, we prepared nanoparticles-loaded PVP films with different concentration of PVP and different dimensions of nanoparticles. Figure 2(a) and Figure 2(b) illustrate the UV-absorption spectra of the PVP-coated film containing gold and silver nanoparticles, respectively. The average dimension of nanoparticles in this film measured to be 30-40 nm. Films of PVP-coated with silver NPs exhibits absorption maxima around 412 nm while PVP-coated gold film shows an absorption peak around 530 nm. These bands demonstrate that the films have roughly spherical nanoparticles as confirmed by SEM images illustrated in Figure 3(a) and Figure 3(b).



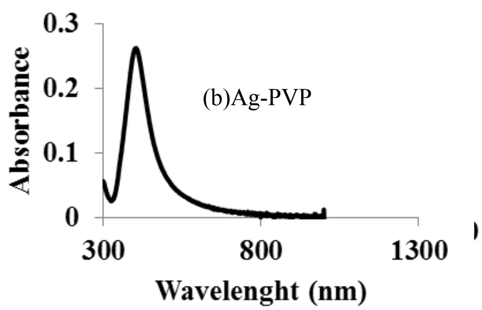
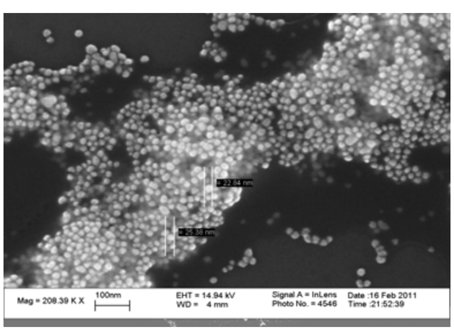
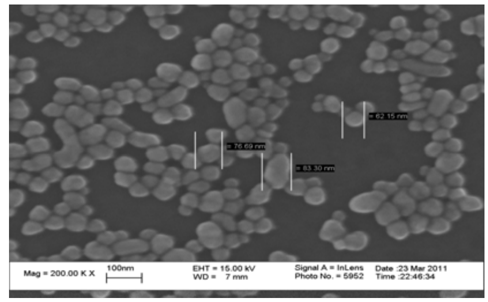


Figure 2: UV-absorption spectra of gold and silver–NPs dispersed PVP solution



(a) Au-NPs



(b) Ag-NPs

Figure 3: SEM images of gold and silver-NPs dispersed PVP solution

Solutions of PVP and NPs are mixed, baked, and finally spun on a 2-inch conductive silicon substrate to make the films. In some cases, a metal layer was required on the substrate before spinning the polymer films. The making of the device utilizes the well-established method of physical vapor deposition (PVD) of the metal on the polymer dielectric film. To make hundreds of nano capacitors devices, a layer of the metal deposition such as titanium is carried out through a meshed plate. Various spinning patterns were developed to produce films with different thickness and loading concentrations to achieve optimum capacitance. Figure 3 illustrate the SEM image of a PVP film loaded with Au@SiO_2 particles. Initial studies revealed that polymers with nanosize metal fillers exhibit percolative behavior, which enhances the dielectric constant of the composite by many folds. As stated earlier, K values of composites can be dramatically increased when loading of the nanofillers (Au@SiO_2) is in the vicinity of the percolation threshold.

We developed a process chain to optimize the use of PVP as dielectric and measured its dielectric constant (K) at 7 at 10 KHz and breakdown field at 130V/μm. K value of 20 and breakdown field of 50V/μm were measured for a dielectric layer with 10% loading of Au/SiO_2 NPs (Table1). Leakage current versus breakdown voltage for Nanodielectric samples of different thickness fabricated with different loadings of nanoparticles is plotted in Figure 4. With increase in loading of nanoparticles, breakdown voltage of the capacitors decreases. Resulting capacitance value of 11.5nF/In2 is in par with commercially available capacitor devices.

Loading of nanoparticles (by volume)	Breakdown field (V/µm)	Dielectric constant (K)
0	130	7
0.056	80	8.1
0.14	81	6.6
0.217	75	4.5
0.64	**33**	**20**

Table 1: Experimental data on metal loading values, Breakdown voltage and Dielectric constants (K) [11]

It is worth mentioning that currently, manufacturers use ceramic based dielectric materials which are hard to manufacture (reproducibility, stability and cost) and have limited flexibility (a requirement in modern printed circuit board technologies) due to high ceramic loading. Our fabricated nanodielectrics have the advantage of ease of fabrication and high flexibility due to the low metal loading.

Further studies are underway on the materials and methods to achieve high k dielectric structures by embedding noble metal-NPs into low dielectric polymers with high breakdown and low loss properties using traditional thin film deposition methods. Very thin layers of Au and Ag are inserted into other polymer like PS and PMMA. These films will be used to fabricate capacitors with high dielectric constant (k) and will be evaluated for capacitance measurements, density and energy trapping nano centers (capacitors). The final results and data will be presented at the conference.

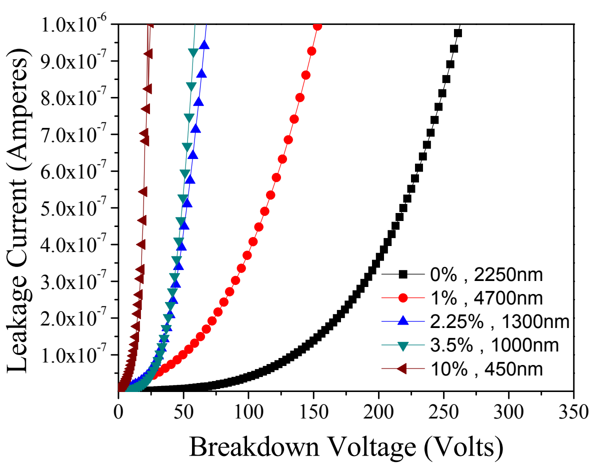


Figure 4: Plots of Breakdown field of Nanodielectrics vs loading of nanoparticles.

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