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Large Capacitive Density in Parallel Plate Nanocapacitors due to Coulomb Blockade Effect

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Abstract: Capacitive density of microcapacitors can be modulated with nanostructured materials via the Coulomb Blockade Effect (CBE). In recent years, the dielectric properties (k and D) of multifarious nanostructured materials have been investigated for application as dielectric material in embedded capacitors. Here we demonstrate that the capacitive response of Ag/PVA nanocomposites on account Coulomb Blockade Effect of nanostructured Ag particles is significant in comparisons to their bulk counterpart and the matrix. The findings regarding the variation of dielectric character on concentration of $AgNO_3$ and the circuit application of the fabricated capacitors are some important ingredients of this investigation.

Keywords: Coulomb Blockade Effect, Dielectric, Nanocomposites.

1 Introduction

The study of Coulomb Blockade Effect (CBE) in metal-polymer nanocomposite materials becomes attractive in recent years as it is the key mechanism of reduced dissipation factor (D) and high dielectric constant (k) of those nanocomposites [1]. When metal particles are embedded in a nonconducting host matrix like PVA, under especial conditions, an exterior electron can tunnel through the particle. If the size of the metal nanoparticle (so called Coulomb island) is tiny, the tunneling electron generate a potential barrier due to the charging energy $e^2/2C$ (where e is the electron charge unit, and C is the capacitance of the metal island) to the further transport of electrons, which is much greater than the thermal capacity $K_B T$ ($K_B$is the Boltzmann constant) at low temperature. Now, if an electron tunnels into a small metal particle it will impede the later coming, for if not so, capacity of this system would have increased and it is restricted by tunnel mechanism. Thus when the charging energy exceeds thermal capacity$K_B T$, the Coulomb Blockade will occur, which impede the charge transfer through the small metal island below a certain threshold voltage and leads to escalate in resistance [2-4]. The plasmonic metal-polymer nanocomposite materials have many fascinating applications viz gate dielectrics in thin film transisors, high charge-storage capacitor and electroactive materials etc. [5, 6]. Previously, ferroelectric ceramic materials with permanent dipole moment like $BaTiO_3$, $BaSrTiO_3$, $PbZrTiO_3$ etc., with high-k in thousands, were used as dielectric materials for decoupling capacitors [7]. However, these materials required very high processing temperature (>600 °C) for frittage and as a result these materials becomes unsuited for the embedded capacitors. However, Polymer dielectric materials are reconcilable with the fabrication of PCB, but the value of dielectric constant of conventional polymers is too low (<5) to accomplish enhanced capacitance density. To augment the dielectric constant of polymer-based materials, the introduction of metal polymer nanocomposite materials is found to be more feasible. These materials are found to be acceptable because of the good processibility and mechanical properties of polymers and the unique characteristic properties like electrical, magnetic or dielectric of the nanofillers makes the materials suitable as dielectric layer in thin film capacitors [8]. Moreover, nanostructured filler particles are preferred for high dielectric constant composite materials because they could help achieve a papery dielectric film which leads to achieve higher capacitance density [9]. There are some reports on incorporation of nano structured metal particles in polymer matrix to produce high k materials. ***Lu et al*** reported that integration of nano Ag particles in the Ag/carbon black/epoxy nanocomposites increased the dielectric constant value and decreased the dielectric loss significantly [1]. ***Feng et al*** investigated the dielectric properties of composite material of Ag nano in PVA host

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and found that the nanocomposite with 20–30 nm Ag particles has a higher resistivity and breakdown voltage than those of its matrix [3]. ***Feng P et al*** fabricated Ag and Ni nanoparticles in polymethylsiloxane matrix with 30% nanofillers and could achieve a dielectric constant of 35 measured at 1 KHz [10]. Some other groups like ***Dhaouadi et al*** [11]**.** ***Mahadevegowda et al*** [12]**,** ***Ling et al*** [13], ***Hu, et al*** [14], ***Francis et al*** [15] etc. have successfully synthesized different nanocomposite materials and applied as dielectric materials. In this work, findings regarding the dielectric behavior of Ag/PVA nanocomposite are reported.

2 Experimental

2.1 Preparation of Ag/PVA Nanocomposite

In this investigation capacitors are fabricated with the dielectric layers of Ag/PVA nanocomposites with $AgNO_3$ concentrations from 5 mmol/L to 45 mmol/L. To compare the dielectric behavior of Ag/PVA nanocomposites are synthesized by reduction of $AgNO_3$ by thermal annealing process [16]. Briefly, $AgNO_3$ solution of different molar concentrations (5 mmol/L to 45 mmol/L) are mixed with 4 % PVA solution in magnetic stirrer and heat treatment at 130 ^{0}C for 20 minutes are given in the reaction mixture. The characteristic parameters of the nanocomposites and the thin films fabricated from it like the surface morphology of the films and the particle size can be tuned by controlling the temperature and time of reaction and the molecular ratio of reactants to matrix. In our earlier works [16], we have optimized the fabrication process by varying all the parameters and the optimized parameters for annealing time and reaction temperature are used in the present study.

2.2 Capacitor Fabrication

To fabricate the thin film capacitor, a glass segment having dimension 20x15x1.5mm^3 is used as substrate and it's cleaned with standard chemical process which is followed by ultrasonication at100 ^{0}C for an hour. The substrate is then kept overnight at 100 ^{0}C to eliminate the contaminants in oven. The bottom aluminum electrode of thickness 500A^0 and width 5mm is deposited on the substrate at very high vacuum (10^{-6} Torr) by thermal evaporation process. A uniform film of the fabricated Ag/PVA nanocomposite is sculpting over the bottom Al electrode by dip coating method. The top Al electrode is deposited over the composite thin film via the same thermal evaporation process at the same deposition conditions. The schematic illustration of the procedure for the fabrication of Ag/PVA nanocomposite based thin film capacitor is shown in fig. 1.

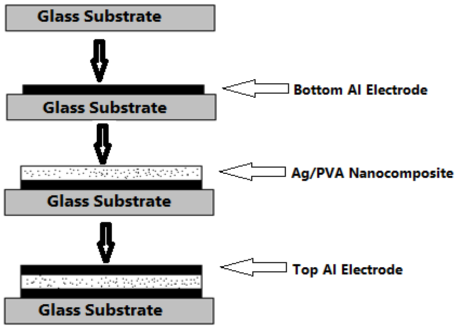

Fig.1: Schematic drawing of thin film capacitor fabrication.

In this investigation capacitors are fabricated with the dielectric layers of Ag/PVA nanocomposites with AgNO3 concentrations from 5 mmol/L to 45 mmol/L. To compare the dielectric behavior of Ag/PVA nanocomposite with that of bulk Ag/PVA composite and the PVA matrix, two more capacitors with these materials as dielectric layer is fabricated by same procedure and conditions as discussed above.

2.3 Characterization

2.3.1 Sample Characterization

The fabricated composite materials under annealed conditions are characterized by UV-VIS Perkin-Elmer Spectrophotometer (LAMDA 950 UV/Vis/NIR) to confirm the formation of nanostructured Ag particles in the host matrix PVA as nanostructured Ag particles can show a strong absorption peak around 400 nm originating from Localized Surface Plasmon Resonance (LSPR). The surface morphology of the fabricated films is investigated through Scanning Electron Microscopy method (LEO 1430VF and LEO 435VP, IITG).

2.3.2 Dielectric Characterization

The characteristics of the fabricated capacitors viz. capacitance and the dissipation factor are investigated by multi-Frequency LCR Meter (LCR 21). The measurements are conducted at room temperature and at frequency of 10 kHz. Selection of frequency at10 kHz is due to the fact that Coulomb Blockade Effect and Interfacial Polarization Effect (IPE) of plasmonic metal polymer nanocomposites are more prominent at low frequency range. In addition, the contribution of interfacial loss is more observable in the high frequency range [1].

Table 1. Variation of paricle size with concentration.

Concentration (mmol/L)	SPR Peak (nm)	Particle size (nm)
5	No SPR Peak	-
15	No SPR Peak	-
25	415	48
35	416	49
45	426.2	55

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3 Results and Discussion

3.1 UV-VIS and SEM Characterization Results

Fig.: 2 show the absorption spectra of the fabricated nanostructured Ag particles in the host matrix PVA. The radiation absorption increases with increasing $AgNO_3$ molar concentration specifying that more nanostructured Ag particles are generated at higher concentration and the increasing Ag nanoparticles resulted in red shift in the LSPR wavelength due to the formation of cluster of Ag nanoparticles [17]. The particle sizes for different concentrations are calculated on the basis of classical Mie Scattering theory [16, 18] and are listed in table 1. In the present study, no prominent SPR peaks are found for the samples with concentrations 5 mmol/L and 15mmol/L. This observation reveals the absence of silver nanoparticles in those samples.

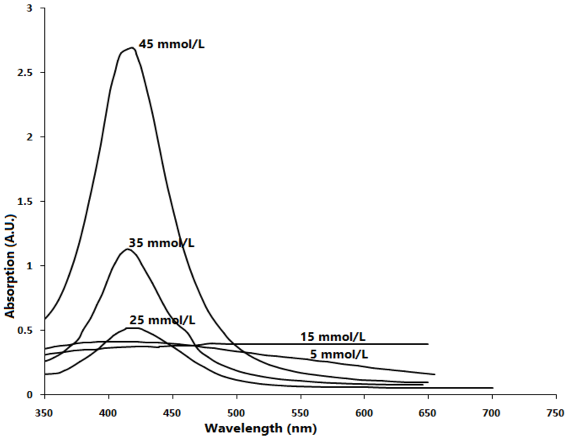

Fig. 2: UV-VIS absorption spectra of Ag/PVA nanocomposite.

The SEM photograph to observe the morphology of the film for sample with concentration of 35mmol/L is shown in figure 3.

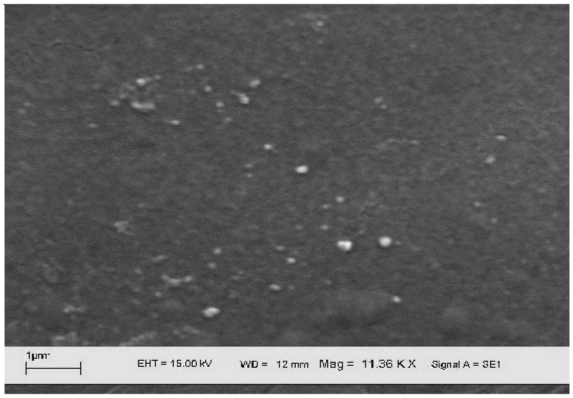

Fig. 3: SEM photograph of Ag/PVA nanocomposite thin film (morphology) (sample with 35 mmol/L molar concentration).

3.2 Capacitor Performance

In this study, capacitors are fabricated with dielectric materials of nanocomposite material with $AgNO_3$ concentrations from 5 mmol/L to45 mmol/L as well as with only PVA matrix and bulk composite materials. The measured dielectric characteristics are given in table 2. The data reveals that Ag/PVA nanocomposite manifest comparatively good capacitive density and low dielectric loss in comparison to its bulk form and the host matrix PVA. The high capacitance density of the nanocomposites is due to charge accumulation at the expanded interface of the interfacial polarization-based composites materials containing nanostructured particles. CBE of nanostructured Ag particles in the PVA is expected to be the reson for low dielectric loss [18]. In this study the capacitive properties are found to vary with $AgNO_3$ concentrations. From 5 mmol/L to35 mmol/L, capacitance density increases while dissipation factor decreases. But at45 mmol/L, the capacitance decreases while dielectric loss increases. The capacitor with $AgNO_3$ concentration of 35mmol/L shows good capacitive character and it is expected that the material attained percolation threshold [19, 20] at 35 mmol/L. The fabricated capacitors with dielectric layer of bulk form of the composite material and only the PVA matrix as shows very low capacitance density and very high dielectric loss which reveals that CBE and IPE are not exhibited for those substances.

To observe the performance of the fabricated thin film nanocapacitors, we perform a simple LCR resonance test with discrete inductor (L=100 mH), resistor (R=200 Ω) and the as-fabricated thin film capacitor with comparatively good capacitive properties. The capacitor with dielectric layer of 35 mmol/L nanocomposite material is tested in series and parallel resonance circuits to investigate its circuit performance. The series and parallel resonance curves are shown in figures 4 and 5 respectively.

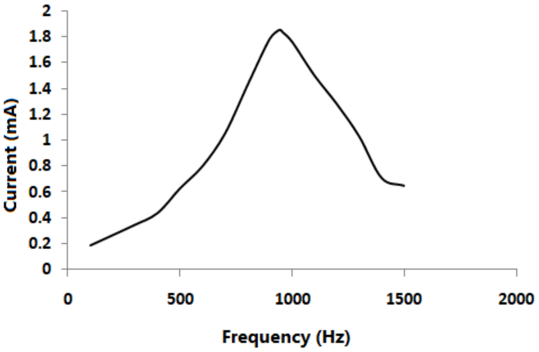

Fig.4: Series resonance curve.

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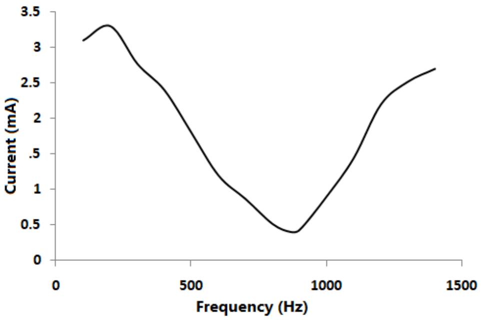

Fig. 5: Parallel resonance curve.

The calculated series resonance frequency is 938.3 Hz (Capacitance density 1154.43 nF/cm^2 i.e C=288 nF) whereas that obtained experimentally is 943 Hz. The percentage of variation is 0.5%. In case of the parallel resonance circuits, a resonance curve is obtained at resonant frequency of 864 Hz and its calculated value is 882.6 Hz. Here the percentage of variation is 2.1%. However, these observations are carried out just after the capacitor fabrication. The performance decreases gradually after few days. The effective preventive approach for this problem might be the encapsulation of the fabricated capacitors with proper encapsulating materials [21].

4 Conclusions

Ag naoparicles of different dimensions are fabricated in the polymer PVA through thermal annealing process and the fabricated nanocomposite films are used as dielectric material layer in thin film capacitors. The CBE and IPE of Ag nanoparticle in PVA matrix enhances the capacitive character of the dielectric by increasing the capacitive density and reducing the dielectric loss. The study of mechanism of Coulomb Blockade Effect in this type of nanocomposite material is our future plan of work.

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