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Core-Shell Percolative Nanodielectric for High Voltage Integrated Capacitors

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Topic: core-shell nanoparticles, high-k composite, dielectric properties

Abstract— High-k dielectric nanocomposites are promising materials to miniaturize integrated capacitors. In this work, we investigate core-shell Metal Polymer Composites (MPC) having nanoparticles (carbon-coated nickel, Ni@C) dispersed in a polymer matrix (Polystyrene). A three-step formulation (desagglomeration, surface functionalization and dispersion in a polymeric matrix) was used with simple sonochemical methods. The original core-shell structure of the MPC results of the grafting of a thin second polymer layer on the carbon coating. Finally, films of MPC were deposited on silicon wafers by spincoating and Metal-Insulator-Metal (MIM) capacitors were fabricated. The dielectric response was investigated by using broadband dielectric spectroscopy. Preliminary results show that below the percolation threshold, MPC with a core-shell structure exhibits twice the dielectric constant of the polymer with similar losses that is encouraging for the future (higher dielectric constant, similar loss).

I. INTRODUCTION

High-*k* polymer nanocomposites, which includes metallic nanoparticles dispersed in a polymeric matrix, are key new dielectrics for ultra-small capacitors in a number of electrical and electronic applications⁽¹⁻³⁾. Nowadays there is currently a fast growing interest in polymer based nanodielectrics because of their flexibility, low cost, easily tunable properties and versatile processing^(4,5).

Dielectric polymers nanocomposites made of ceramic or metallic particles embedded into an insulating polymer matrix are among the most promising systems. This approach allows to obtain a new class of materials in which its possible to exploit the electrical features of the fillers materials in combination with the easy processing of polymers⁽⁶⁾. These materials exhibit a large increase of the dielectric permittivity in the proximity of the percolation threshold. The enhanced polarizability of the nanocomposite can be explained as the formation of locally large micro-capacitors effect, which contribute to increase the dielectric constant of material⁽⁷⁻⁹⁾. Currently, this technology suffers from a weakness due to the substantial increase of dissipation factors around percolation threshold. In practice, a lack of control on the dispersion order of the nanoparticles in the polymeric matrix generates resistive contacts between the metallic nanoparticles.

Most significant challenge in the field consists in obtaining a high permittivity value related to a low dissipation factor in the frequency ranges of interest. In this view, only a refined structural control of the nanoparticles within the polymeric matrix guarantees the achievement of the desired electrical properties.

The aim of this work is to establish a wafer-scale film fabrication process of metal polymer nanocomposites (MPC) based on commercial carbon coated nickel nanoparticles Ni@C. This work focuses the desagglomeration of the nanopowder, the surface functionalization of the nanoparticles with the aim to create a core-shell structure by grafting a thin polymer layer (few nm) on the carbon coating and the dispersion in a polymeric matrix. This three-step formulation is based on simple sonochemical methods. The core-shell structure of the MPC is intended to get greater control of interparticulate spacing distribution and to finely adjust the filling factor below the critical electrical percolation threshold where the dielectric constant be substantially enhanced with limited electrical dissipation.

II. EXPERIMENTAL PART

A. Materials

Commercial Carbon-coated nickel nanoparticles (Ni@C) are supplied by Nanostructured & Amorphous Materials, Inc. (20 nm). The polymer shell Pyr-PS₁ is a pyrene-terminated polystyrene (2.8 kg/mol) from Polymer Source, and the matrix PS₂ is a polystyrene (280k Mw) from Sigma-Adrich. The solvent used is Propylene glycol methyl ether acetate (PGMEA) from MicrodepositTM EC Solvent and used as received.

B. Preparation

The objective is to produce processable films of nanocomposite, from raw powder materials. Directly mixing the nanoparticles (Ni@C) and the polystyrene matrix PS₂ fails, as inhomogeneous dispersion and large dewetting zones form. Hence, functionalization of the nanoparticles is required. A soft stacking of pyrene-terminated polystyrene Pyr-PS₁ was used to coat the nanoparticles surface. The flow chart to obtain the casting solution of Ni@C/Pyr-PS₁/PS₂ blend is discussed. The high power ultra-sonication of the suspension of nanoparticles in PGMEA breaks the big agglomerates of the nanopowders. The dispersion is sonicated in 3 different steps of 10 minutes at 100 W (VCX500 ultrasonic processor Sonics). Afterwards the Ni@C nanoparticles are functionalized by the Pyr-PS₁. This step requires a further step of 10 min at the same power by adding 20 mg of polymer. Finally, PS₂, previously dissolved in PGMEA at a concentration of 0.3 g/ml, is added. The stabilized suspensions of Ni@C/Pyr-PS₁/PS₂ in PGMEA is used for spin-coating within the 5 minutes after the last sonication.

C. Ni@C film deposition

Nanocomposites films are spincoated on 4-inches wafers. The targeted thickness of the film is in the range of 10 μm . This was achieved by successive spincoating processes. The first coating is set at 1000 rpm with an acceleration of 5000 rpm^{-1} then the successive steps are set at 500 rpm with an acceleration of 500 rpm^{-1} . For each deposition step, 2 mL of the formulated nanocomposite resist is dropwise spread on the wafer surface. After each spincoating, the films are annealed at 150 $^{\circ}\text{C}$ for 30 min on a hot plate for solvent evaporation. Films deposited onto silicon wafers with a 500 nm thick layer of thermal oxide were used for characterization purpose while films deposited on metallized wafers Si/SiO₂ (500nm) /Cr (5-10nm)/Au (200nm) are dedicated for MIM capacitors measurements.

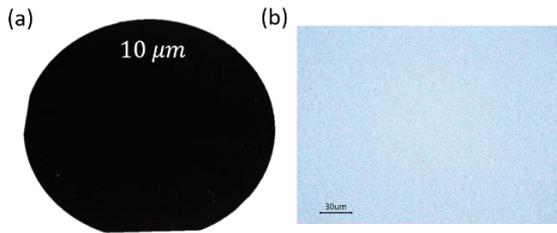


Figure 1 – (a) Pictures of Ni@C/Pyr-PS₁-PS₂ dielectric composite film, (b), Optical surface analysis (b).

For these last samples, the 30 nm top electrode is achieved by sputtering Gold through a shadow mask on the film surface. All deposited films are macroscopically uniform with a thickness in the 10 μm range. (Figure 1 (b)).

III. RESULTS AND DISCUSSION

A. Nanocomposites resist characterization

The stability of the Ni@C dispersions was investigated using the variation of the mean size distribution of the suspension measured using Dynamic Light Scattering (Zetasizer Ultra, Malvern Panalytical).

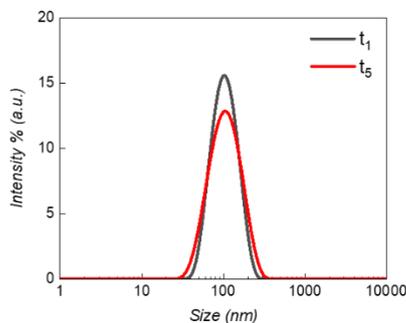


Figure- 2 DLS measurements of suspension of Ni@C nanoparticles in PGMEA at 0.0875 mg/ml after ultrasonication.

Dilution was set at 0.0875 mg/ml in order to ensure precise DLS measurements. A total of 5 successive measurements of the Scattered light was planned that covers a total sedimentation duration of 20 minutes in backscatter mode. No significant differences in the correlation curves was obtained for the first and the last scan are detected. It means

that the nanoparticles dispersion is stable. In Figure 2, the measured size distribution (in intensity) of the dispersed nanoparticles is centered at 100 nm. No significant variation in the NP size is reported so negligible sedimentation occurs.

B. MIM capacitors performances

The dielectric properties of the nanocomposite at a 0.025 g/ml loading of Ni nanoparticles was determined by measuring the impedance of the MIM capacitor with an impedance analyzer (Novocontrol Alpha-A Analyzer). The AC voltage was set at 3 V and the scan recorded in a frequency range of 100 Hz–10⁶ Hz. The diameter of the top electrodes is 2.5 mm and the thickness of the deposited film was measured at 13 μm by profilometry. Raw impedance measurements were conversely post processed in order to obtain the dielectric permittivity.

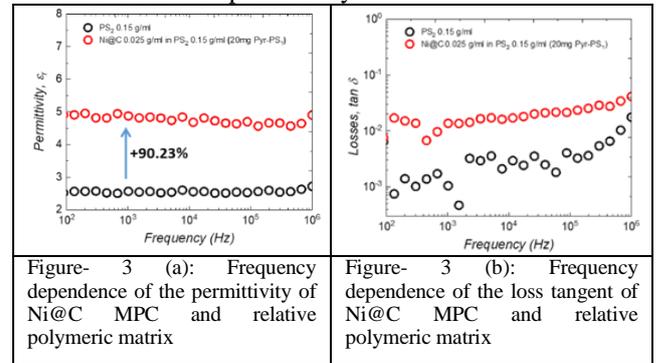


Figure- 3 (a): Frequency dependence of the permittivity of Ni@C MPC and relative polymeric matrix

Figure- 3 (b): Frequency dependence of the loss tangent of Ni@C MPC and relative polymeric matrix

Figure 3 (a) presents obtained dielectric constant for this film. One can see that the dielectric constant at 1 kHz increases from 2.5 to 4.7 when this low filler contents is added to the PS₂ film (90 times higher). Meanwhile the recorded values of the loss angle, in this frequency range, remain relatively low (0.02 at 1k Hz). The high-*k* material developed in this study exhibits low losses, making it suitable for realistic applications.

IV. CONCLUSION

We report a wafer-scale film fabrication process of core-shell MPC film for MIM capacitors based on functionalized carbon-coated nickel nanoparticles Ni@C using simple sonochemical methods and spincoating. MIM capacitors on silicon wafers were fabricated using this process.

Particles size, filling ratio and dielectric properties have been investigated. Below the electrical percolation threshold, MPC with the core-shell structure exhibits twice the dielectric constant of the polymer with similar losses that is encouraging for the future in order to rich high dielectric constant with controlled loss closer to this limit.

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