THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N°. 4 - 2019, ISSN 2668-4748; e-ISSN 2668-4756
Article DOI: https://doi.org/10.35219/mms.2019.4.07

DIELECTRIC CHARACTERIZATION OF S_iO_2-PMMA ORGANIC – INORGANIC HYBRID THIN FILMS

Elena Emanuela HERBEI
"Dunarea de Jos" University of Galati, Romania
e-mail: elena.valcu@ugal.ro

ABSTRACT

For the research presented in this paper, hybrid organic-inorganic materials were prepared using a modified sol-gel reaction.

Hybrid organic-inorganic compounds were synthesized in ethanol using methylmethacrylate (MMA), SiO_2 nanoparticles, and 3-trimetoxi-silil-propil-methacrylate (TMSPM) as coupling agent. For the deposition of thin films, the spin-coating method was used.

The electrical measurements of dielectric thin films were done using a metal-insulator-metal (MIM) devices fabricated to study the dielectric constant of the films as function of frequency (measured at 1 MHz). Electrical results show a weak trend of the dielectric constant of the hybrid films with different MMA molar ratio. More importantly, the PMMA-SiO_2 hybrid films showed a higher dielectric constant than SiO_2 and PMMA layers, due to the presence of additional C-O-C bond. For the calculation of dielectric permittivity, the thickness of thin films was measured using cross-section SEM micrographs and the value of dielectric permittivity was calculated using electrical capacitance formula.

KEYWORDS: thin films, dielectric, PMMA-SiO_2, nanoparticles

1. Introduction

Thin-film transistors (TFTs) based on hybrid materials present great interest for different potential applications in portable devices, sensors, radio-frequency (RF) identification tags, smart cards, and backplane circuits for active matrix displays and flexible electronics among others. In the latest years, the technology has been focused on the development of new materials, which can be easily processed at low temperature in different large-area of applications, which are compatible with different substrates for transparent flexible electronics.

The dielectric gate used in flexible devices requires a lot of conditions to be promising materials.

The transistor parameters critically depend not only on the thickness and the dielectric properties of the gate insulator but also on the interface formed between dielectric and semiconductor layers, where the trapped charge has strong influence on the device electrical behaviour [1].

Recently, SiO_2, TaO_2, Ta_2O_5, ZrO_2 and HfO_2 transition metal oxides were demonstrated as premise for high-k dielectric materials in submicron range technology [2, 3].

The SiO_2-PMMA hybrid system was synthesized using the sol-gel method [4, 5]. The sol-gel process is one of the most convenient methods to achieve the proper linking between the organic and inorganic phases at the molecular scale. Furthermore, the sol-gel route is suitable to produce a multi-functional hybrid.

The hybrid materials could provide the following advantages over organic polymers for optical waveguide applications: (1) The incorporation of the inorganic moiety into polymer matrix could improve the thermal and mechanical properties; (2) the incorporation of inorganic moiety decreases the C-H bonding density in the waveguide materials and thus reduces the optical loss; (3) the large polarizability difference between the organic and inorganic moieties possibly induces an increase of the anharmonicity of the C-H bond and thus the NIR spectra could be shifted for the optical window of the used light source [6].

Although the SiO_2 thin films are limited in utilisation as dielectric gate due to the band gap which increase to 9eV. In different condition of utilisation, the thin film became semiconductor, that is why is used in combination with MMA that in the presence of UV light it turns into in PMMA. The presence of new C-O-C bond decrease the energy band gap. To have dielectric properties the thickness of thin films must be under 100 nm. Here is report the first attempts of fabrication bellow 160° C of hybrid thin films containing silica oxide nanoparticles by modified sol-gel route in which a 3-trimetoxysilylpropyl methacrylate (MPS) coupling agent is used to have a good interaction between the SiO_2 nanoparticles and methylmethacrylate monomer. SiO_2 was used as precursor for the inorganic (oxide) part and methyl methacrylate (MMA) as precursor of the organic polymeric component. The molar ratio between SiO_2 and the polymethyl methacrylate was adjusted to ensure the adherence, flexibility and good dielectric properties of the films.

2. Experimental

2.1. Preparation of sols and thin films

SiO_2 nanoparticles, 3-trimetoxysilylpropyl methacrylate 98% (MPS), methylmethacrylate 99% (MMA) and absolute ethanol 99.99% (Et-OH) purchased from Sigma-Aldrich were used for the preparation of hybrid films.

For the sol preparation, the silicon dioxide was dissolved into absolute ethanol at room temperature. The MPS coupling agent and the methyl methacrylate monomer was added successively.

For the dielectric film deposition, two sol compositions corresponding to SiO_2:MMA molar ratios of 1:1 and 4:1 were prepared (Table 1). Each sol was aged at 50 °C until it became transparent and provided good viscosity for the film deposition. The resulting homogeneous solution was spin-coated onto cleaned n-doped silicon substrates, covered by sputtering with a tantalum layer of 100 nm thickness. The post-deposition treatment of films consisted in 10 minutes hot plate thermal treatment at 160 °C and exposed at UV radiation (λ = 254 nm) emitted by an H 466.1 UV lamp. For electrical characterization, aluminium contacts (~300 nm in thickness) with different areas were evaporated through a shadow mask on top of the hybrid dielectric film.

Table 1. *Investigated samples*

Sample symbol	**Molar ratio** SiO_2:PMMA/number of layers	**Thickness of the film** (nm)	**Capacitance, C** (F) *10^{-10} (medium value)	ε_r
P1	(1:1) /1 layer	170	4.3	1.9
P2	(1:1) / 2 layers	330	4.1	4.7
P3	(4:1) / 1 layer	220	3.5	2.3
P4	(4:1) / 2 layers	400	3.2	4.5

2.2. Thin films characterization

The surface and cross-section morphology of the hybrid films were investigated by scanning electron microscopy (SEM) using an EOL JSM-7500F/FA microscope and by high resolution transmission electron microscopy (HR-TEM) using a Tecnai TM G2 F30 S-TWIN microscope equipped with a STEM/HAADF detector.

The I-V and C-V curves of the hybrid films were measured by including them into a Metal-Insulator-Metal (MIM) structure (Fig. 1), using Agilent 4156 and HP 4277A Analysers, respectively, at 1 MHz.

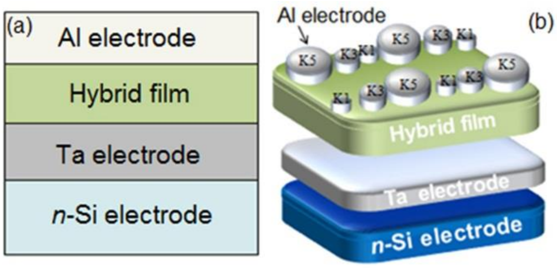


Fig. 1. *Schematic representation (a, b) of MIM structure used for the measurement of I-V and C-V characteristics of thin films*

3. Results and discussion

The hybrid thin films of SiO_2-PMMA, deposited with 1 and 2 layers had the thickness value between 250 and 400 nm, respectively. SEM images onto thin films surface, deposited with one layer shows a non-homogenous, discontinuous aspect regarding the distribution of nanoparticles, a high roughness of the

N°. 4 - 2019, ISSN 2668-4748; e-ISSN 2668-4756
Article DOI: https://doi.org/10.35219/mms.2019.4.07

film consisting of agglomerates porous and not uniform of spherical particles embedded in the polymeric mass. In these agglomerates formed by the embedding of spherical SiO_2 we can distinguish the spherical form of initial nanoparticles.

The roughness determined by the presence of nanoparticles affects the structure of aluminium electrodes deposited by thermal evaporation for electrical measurements (Figure 2-6).

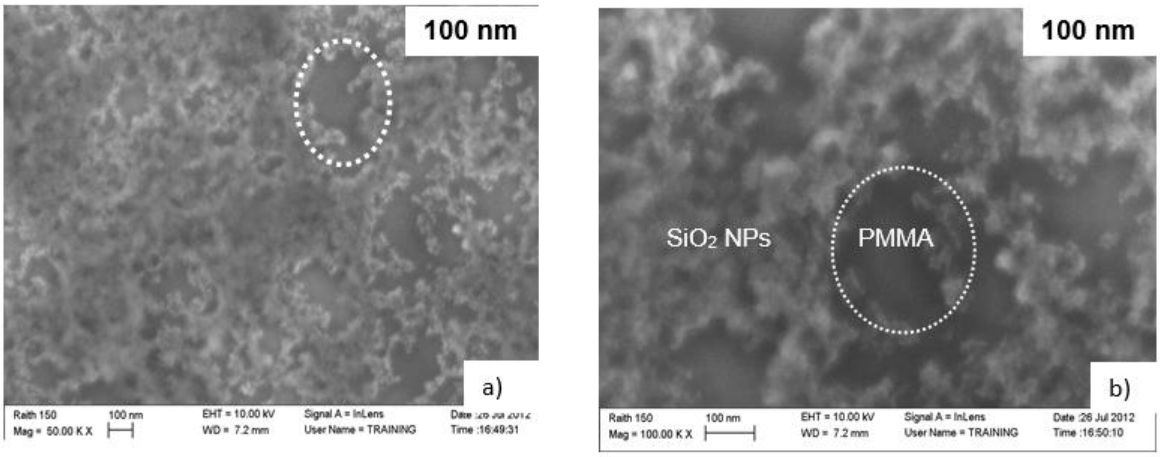


Fig. 2. *SEM images top-view of SiO_2-PMMA (1:1) 1 layer (a) and detail (b)*

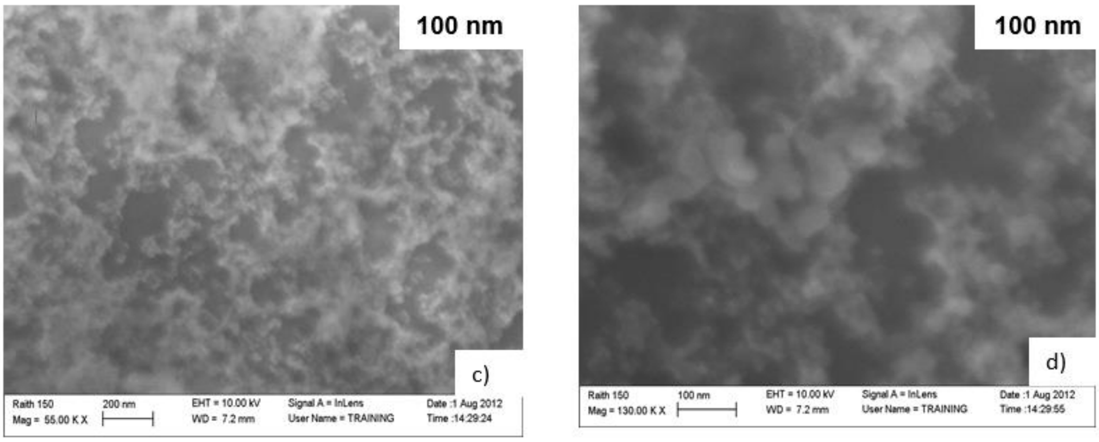
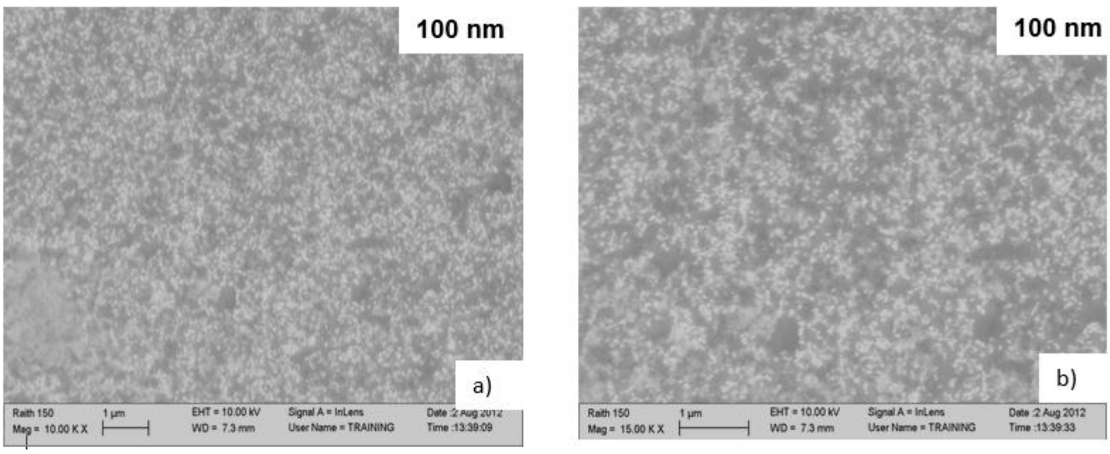


Fig. 3. *SEM images top-view of SiO_2-PMMA (4:1) 1 layer (a) and detail (b)*



N°. 4 - 2019, ISSN 2668-4748; e-ISSN 2668-4756
Article DOI: https://doi.org/10.35219/mms.2019.4.07

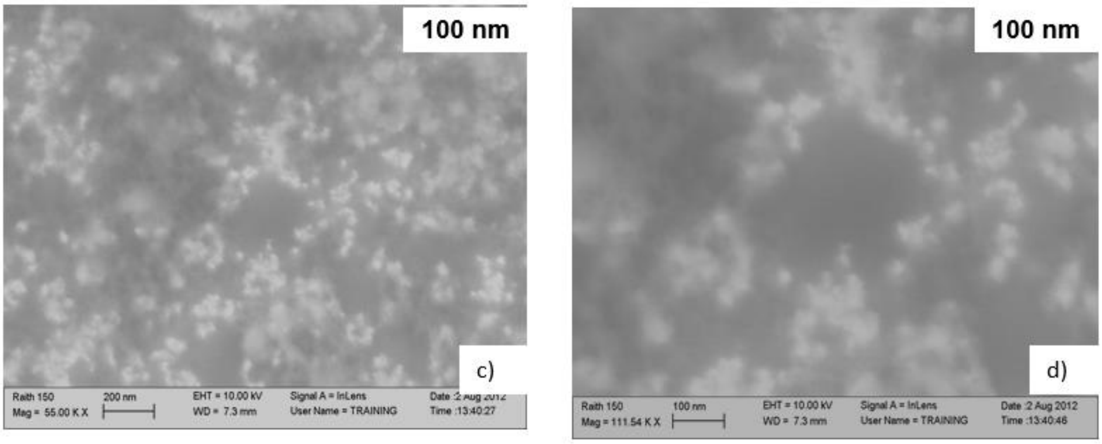


Fig. 4. *SEM images top-view of SiO_2-PMMA (1:1) 2 layers (a) and detail (b-d)*

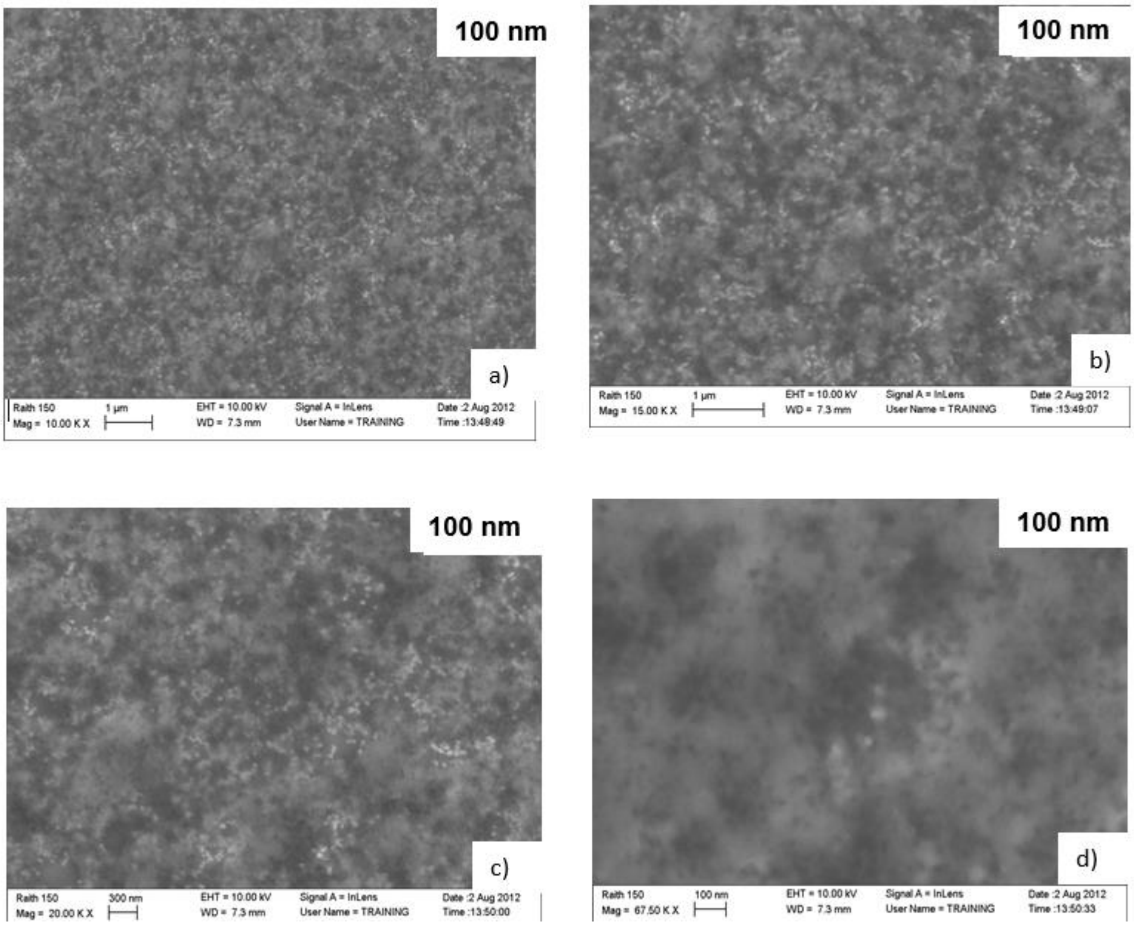


Fig. 5. *SEM images top-view of SiO_2-PMMA (4:1) 2 layers (a) and detail (b-d)*

The SiO_2-PMMA films deposited with two layers, 1:1 and 4:1 molar ratio shows a higher degree of coating with oxide nanoparticles of substrate surface. However, the increase of the nanoparticle concentration caused the porosity and non-uniformity in the film thickness (Fig. 6).

As we can observe in Fig. 6, the increase of roughness affects the Al electrodes structure deposited onto thin film surface by the thermal evaporation for the electrical properties.

The thickness of the films is thinner for (1:1) than for (4:1) molar ratio, about 200 and 470 nm, respectively, because the higher concentration of SiO_2

THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N°. 4 - 2019, ISSN 2668-4748; e-ISSN 2668-4756
Article DOI: https://doi.org/10.35219/mms.2019.4.07

provides higher sol viscosity and roughness. For both films, the SEM images show a morphology without phase separation between the organic and inorganic components. The roughness of the thin film layer determines the irregularity of Al electrodes.

Fig. 7 shows the I–V characteristics of the investigated films, at gate voltages from 4 to +4 V. The leakage current density is ranging from 10^{-6} to 10^{-1} A/cm^2 and from and 10^{-6} to 10-2 A/cm^2 in the case of 1:1 and 4:1 molar ratio, respectively. Further studies are considered to correlate the dielectric behaviour of films with the effect of temperature and duration of post-deposition thermal treatment.

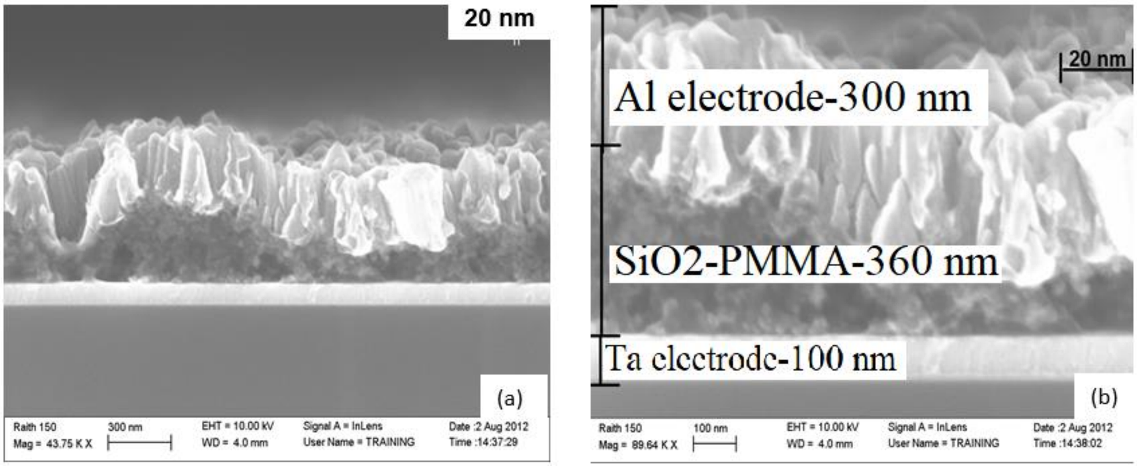


Fig. 6. *SEM images top-view of SiO_2-PMMA (4:1) 2 layers (a) and detail (b)*

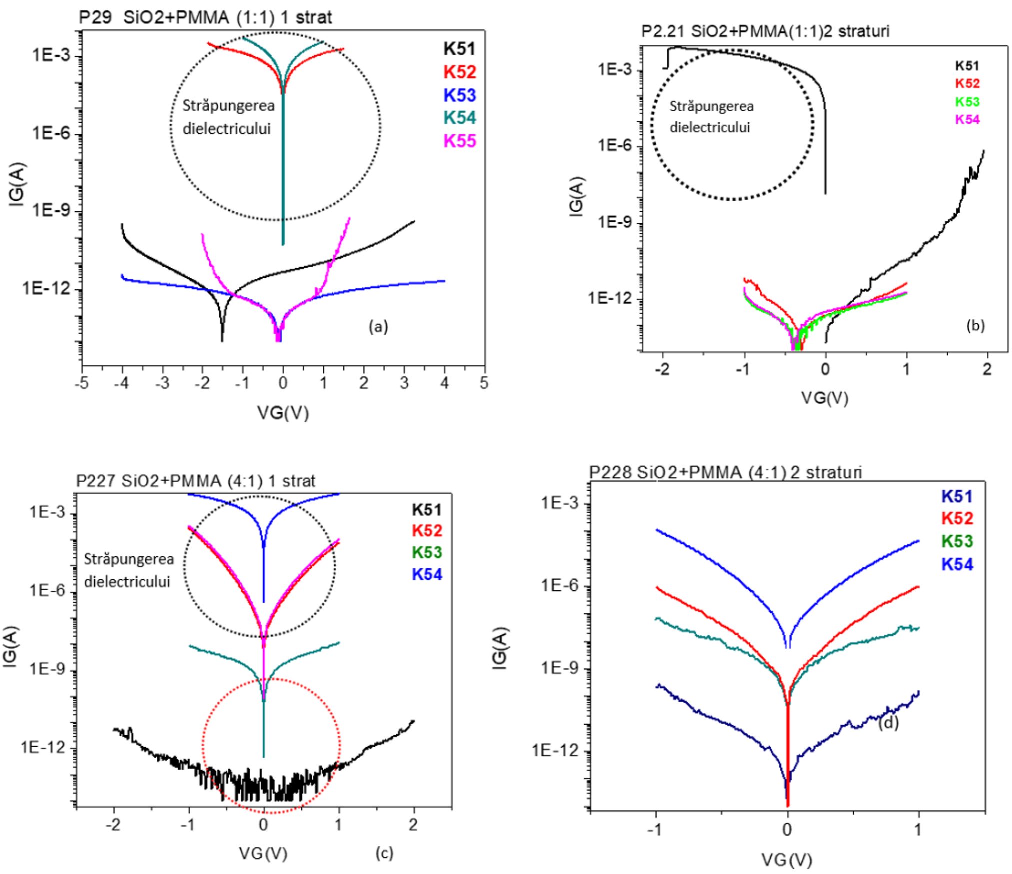


Fig. 7. *I-V characteristics for SiO_2:PMMA-1:1 (1 layer and 2 layers) and SiO2-PMMA -4:1 (1 layer and 2 layers)*

From the C–V curves of the investigated films, the dielectric constant was calculated. The values of 1:1 and 4:1 molar ratio hybrid film was determined from the C–V measurements in the voltage range from -15 to +15 V, at 1 MHz. The dielectric permittivity of a material is proportional to its electronic polarization. Materials with polar groups (i.e. C=O, OH) usually have large dielectric constants due to the orientation of their electrical dipoles in the electric field. Taking also into consideration the fact that the hydroxyl group has the highest molar polarization [4, 20], by adding different molar ratio of the precursor, the dielectric constant increases from about 1.9 to 4.5 with increasing the SiO_2:MMA ratio from (1:1) to (4:1).

4. Conclusions

SiO_2:PMMA hybrid dielectric thin films for flexible electronics were successfully prepared by sol-gel methods below 200 °C. SiO_2 nanoparticles were embedded in amorphous matrix and the dielectric properties were determined for films with 1:1 and 4:1 molar ratio. The use of 3-trimetoxysilylpropyl methacrylate (MPS) as coupling agent improves the compatibility between the organic and inorganic phases, it allows obtaining homogeneous and roughness thin films without phase separation. The I-V curves show a leakage current between 10^{-12} and 10^{-9} A, and a constant capacitance in bias range ± 15 V. Dielectric constant of 4.5 was obtained for the hybrid films with 4:1 molar ratio. Further investigation will be continued to establish the conditions required to prepare stoichiometric nanocrystalline SiO_2 phases from alkoxide precursor embedded into polymer matrix.

References

[1]. Choi C. G., Bae B.-S., *Organic-Inorganic Hybrid Materials as Solution Processible Gate Insulator for Organic Thin Film Transistors*, Org. Electron, 8, p. 743-748, 2007.

[2]. Sangwan V. K., Ortiz R. P., Alonso J. M. P., Emery J. D., Bedzyk M. J., Lauhon L. J., Marks T. J., Hersam M. C., ACS Nano, 6 (8), p. 7480-7488, 2012.

[3]. Gyeong-Su P., Young B. K., Seong Y. P., Xiang S. L., Sung H., Myoung-Jae L., Man C., Nature Communications, 4, 2013.

[4]. Almaral-Sanchez J. L., Rubio E., Mendoza-Galvan A., Ramirez-Bon R., *Red colored transparent PMMA-SiO_2 hybrid films*, J Phys Chem Solids, 66, p. 1660-1667, 2005.

[5]. Alvarado-Rivera J., Munoz-Saldana J., Castro-Beltran A., Quintero-Armenta J. M., Almaral-Sanchez J. L., Ramirez-Bon R., *Hardness and wearing properties of SiO_2-PMMA hybrid coatings reinforced with Al_2O_3 nanowhiskers*, Phys Stat Sol, 11, p. 4254-4259, 2007.

[6]. Chia-Hua Lee, Wen-Chang Chen, *Synthesis and Optical Characteristics of Trialkoxycapped Poly(methyl methacrylate)-Silica Hybrid Films*, Tamkang Journal of Science and Engineering, vol. 6, no. 2, p. 73-80, 2003.

[7]. Morales-Acosta M. D., Ma Quevedo-Lopez, Rafael Ramírez-Bon, *PMMA-SiO_2 hybrid films as gate dielectric for ZnO based thin-film transistors*, Materials Chemistry and Physics, 146, (3), p. 380-388.

[8]. Morales-Acosta M. D., Alvarado-Beltrán C. G., Quevedo-López M. A., Gnade B. E., Mendoza-Galván A., Ramírez-Bon R., *Adjustable structural, optical and dielectric characteristics in sol-gel PMMA-SiO_2 hybrid films*, Journal of Non-Crystalline Solids, volume 362, p. 124-135, 15 February 2013.