

DIELECTRIC PMMA THIN LAYERS OBTAINED BY SPIN COATING FOR ELECTRONIC APPLICATIONS

Elena Emanuela HERBEI

Interdisciplinary Research Centre in the Field of Eco-Nano Technology and Advance Materials CC-ITI, Faculty of Engineering, "Dunarea de Jos" University of Galati, 47 Domneasca, 800008 Galati, Romania
e-mail: elena.herbei@ugal.ro

ABSTRACT

Thin polymeric films with dielectric properties become a very important part of today's devices, being indispensable in industry, electrical applications and not only. Nowadays polymeric materials have attracted attention in academic and industrial research due to the miniaturization at the micro and nanoscale of different electronic devices. Polymers in general are used for their light weight, good mechanical strength, dielectric properties, and optical properties, which make them multifunctional materials.

This paper presents research on polymethyl methacrylate (PMMA) thin films obtained by the sol-gel method. The optimization of thin film PMMA layers has been a problem due to the importance of using the polymer in the different electronic domains. Thin films of PMMA with different thicknesses were deposited onto glass and silicon wafers in order to measure dielectric properties. For dielectric properties, the PMMA thin layer was inserted in a metal-insulator-metal structure (MIM). In order to observe the morphology and roughness of thin film, optical microscopy, scanning electron microscopy and atomic force microscopy have proceeded.

The dielectric constant (k) was calculated using the electrical capacitance formula. The I-V and C-V curves showed a dielectric behavior with a leakage current between 10^{-11} and 10^{-8} A and a constant capacitance in the bias range ± 5 V.

KEYWORDS: thin films, polymeric films, dielectric properties, polymethyl methacrylate

1. Introduction

The development of TFTs devices based on thin layers of polymer compounds by sol-gel became a good solution and gain special attention to the low cost obtaining.

Because of its low cost and high output like transparency, thermal stability, electrical insulation, and mechanical resistance, the thin film layer of PMMA has sparked interest for use as an insulator in electronic and optoelectronic devices [1]. It has also good optical properties (transparency in a wide range of wavelengths from near ultraviolet to near-infrared) [2, 3]. For the preparation of polymeric thin films, different types of PMMA in anisole [4] toluene, DMF [5], chloroform [6], benzoyl peroxide (BPO 98%) to start the polymerization of MMA and to obtain PMMA solution at 70 °C [7] or alcoholic solution [8],

or with the value of molecular weight from 495 to 996 Kw were used. There are several methods in order to obtain thin layers of PMMA as ALD [9, 10], ink-jet printing [11] but the most used is sol-gel process due to its versatility and low-cost method [10, 12].

In order to use PMMA as dielectric gate in TFTs requires a lot of conditions to be promising materials.

Transistors parameter depend on the interface formed between dielectric and semiconductor layers, where the trapped charge has a strong influence on the device's electrical behavior [13].

The low leakage current density is highly desirable for the fabrication of stable TFTs for low-power consumption electronic devices [7, 14].

In different papers [3, 15, 16], the capacitance density of the polymeric dielectric layer was measured on the same MIM device in the frequency

range from 1 kHz to 1 MHz and the results are promising in order to use PMMA gate in TFTs.

In this paper, we have investigated a PMMA anisole solution to prepare thin films by spin coating method, one of the most used sol-gel method, for the simple and low-cost process. We fabricated a MIM device, represented by Al top-electrode/PMMA films/Si/Ta layer substrate, to study the dielectric properties of the obtained polymeric thin films and to calculate their dielectric constant.

2. Experimental

2.1. Preparation of sols and thin films

PMMA (495 kw) in anisole was purchased from MICRO CHEM and used for the preparation of hybrid films. Polymeric solution (25%) was prepared by magnetic stirrer at room temperature. First the solution was deposited on glass substrate to have one

and two layers of PMMA with 100-150 nm thickness. The deposition was done by spin-coating method at 2000 rpm for 30 seconds.

After optimisation of the thickness the solution was spin coated for 30 seconds in air, onto the n-doped Si substrates covered with a layer of 100 nm tantalum (Figure 1a). The as-deposited films were thermally treated on hot plate at 120 °C for 30 minutes.

Before film deposition, the substrates were cleaned using the following procedure: washed in water for three times, dipped in isopropanol for 1 minute and cleaned with water, dried with nitrogen stream and hotplate for 5 minutes at 120 °C. To have a MIM structure, after PMMA deposition (Figure 1b), metallic aluminium contacts (Figure 1c) were thermally evaporated through a shadow mask with different areas (180, 320 and 680 μm diameters) resulting a multi-layer structure (Figure 2).

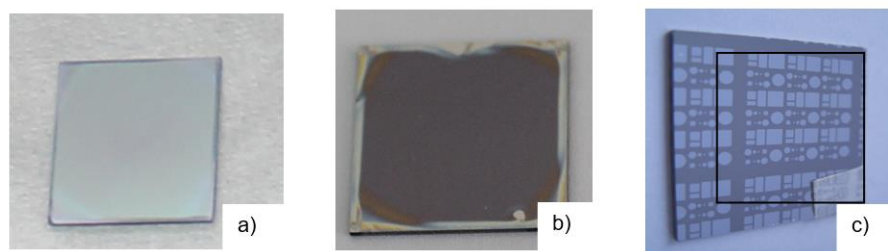


Fig. 1. a) Si substrate with Ta (100 nm); b) PMMA layers on Si substrate; c) MIM structure

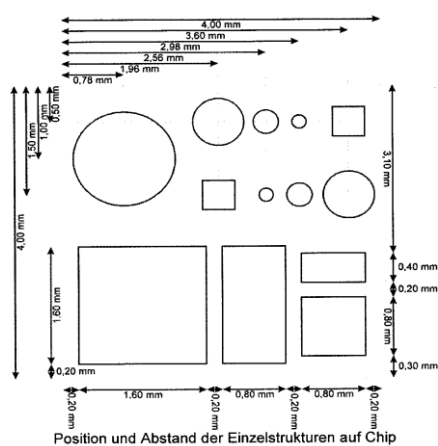


Fig. 2. Schematic representation of electrodes areas

2.2. Thin films characterization

The roughness was investigated with atomic force microscopy and for surface and cross-section morphology of the polymeric thin films was used a

scanning electron microscopy (SEM) using a EOL JSM-7500F/FA microscope.

The I-V and C-V curves of the hybrid films were measured by including them into a Metal-Insulator-Metal (MIM) structure (Fig. 3), using Agilent 4156 and HP 4277A Analysers, respectively, at 1 MHz.

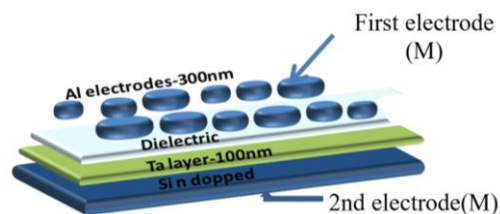


Fig. 3. Schematic representation (a, b) of MIM structure used for the measurement of I-V and C-V characteristics of thin films

3. Results and discussion

In Figure 4a and 4b are presented the AFM and SEM images of PMMA layer by comparison. The

structure of film is homogenous the entire surface having a specific relief as a honeycomb do to the high molecular weight. The thermal treatment applied for stabilisation is modifying the structure.

From the AFM roughness we can observe that is between 15 to 25 nm (Figure 5).

Figure 6 shows the I-V and C-V characteristics of the investigated films, at gate voltages from 4 to +4 V. The leakage current density is 10^{-6} to 10^{-1} A/cm². Further studies are considered to correlate the dielectric behaviour of films with the effect of temperature, number of layers and duration of post-deposition thermal treatment.

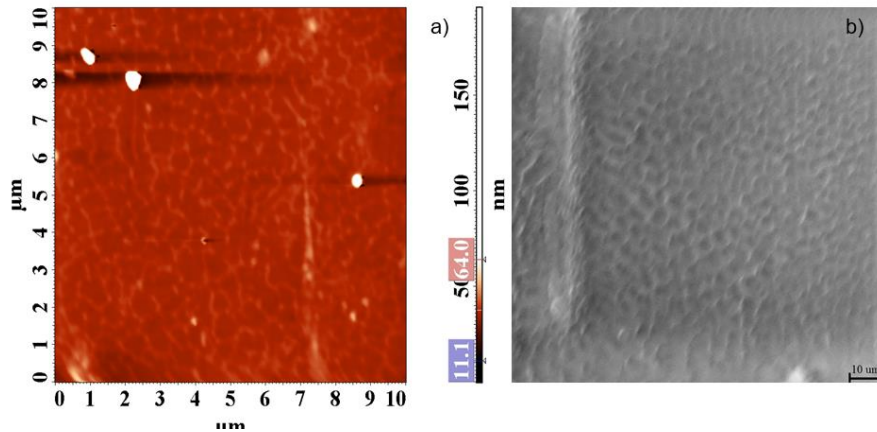


Fig. 4. a) AFM and b) SEM images of PMMA layer

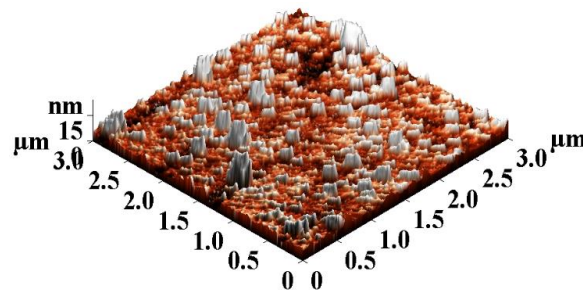


Fig. 5. AFM image of a central PMMA layer

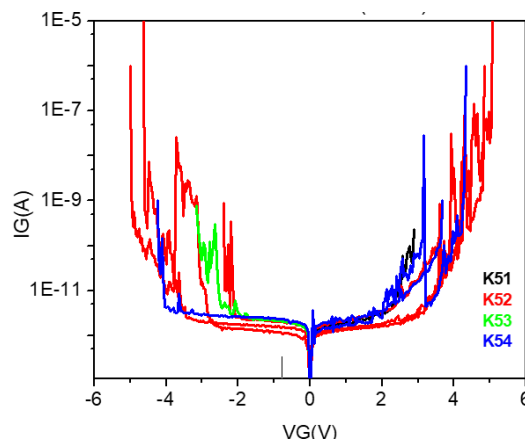


Fig. 6. I-V characteristics for PMMA layer

From C-V (Figure 7) curves of the investigated PMMA film, dielectric constant was calculated. The values were determined in the voltage range from -55

to + 55 V, at 1 MHz. The dielectric permittivity of a material is proportional to its electronic polarization.

The measurements showed a dielectric behaviour enough homogenous without breakdown leakage. The values of dielectric constant measured

on different electrodes area varied from 3 to 4 as in Table 1.

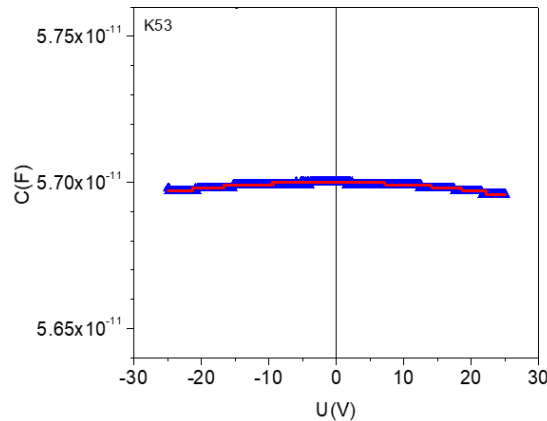


Fig. 7. C-V characteristics for PMMA layer

Table 1. Electrical capacitance and dielectric values of PMMA layer for different electrodes area

Electrode area *10 ⁻⁴ cm ²	Electrical capacitance C (F) *10 ⁻¹¹			ε _r
	Area 1	Area 2	Area 3	
2.054 (K1)	42.32	42.04	40.67	3
8.043 (K2)	1.536	1.464	1.504	3.2
32.17 (K3)	5.511	5.295	5.291	3.8
128.7 (K4)	0.2049	0.1972	0.1971	4

4. Conclusions

PMMA dielectric thin films for flexible electronics were successfully prepared by sol-gel methods below 200 °C. The I-V curves show a leakage current between 10⁻¹¹ and 10⁻⁸ A and a constant capacitance in bias range ± 4 V. Dielectric constant varying from 3 to 4 was obtained for different electrodes area films. Further investigation will be continued to establish the variation of dielectric constant on different point of thin film of the sample.

References

[1]. Nassier L. F., Shinen M. H., *Study of the optical properties of poly (methyl methacrylate) (PMMA) by using spin coating method*, Mater. Today Proc., vol. 60, p. 1660-1664, doi: 10.1016/j.matpr.2021.12.213, 2022.
 [2]. Valcu E. E., Musat V., Jank M., Oertel S., *Sol-gel preparation of ZrO₂-PMMA for thin films transistors*, Rev. Chim., vol. 65, no. 5, p. 574-577, 2014.
 [3]. Muşat V., et al., *Low-Temperature and UV Irradiation Effect on Transformation of Zirconia-MPS nBBs-Based Gels into Hybrid Transparent Dielectric Thin Films*, Gels, vol. 8, no. 2, doi: 10.3390/gels8020068, 2022.

[4]. Shekar B. C., Sathish S., Sengoden R., *Spin coated nano scale PMMA films for organic thin film transistors*, Phys. Procedia, vol. 49, no. 0, p. 145-157, doi: 10.1016/j.phpro.2013.10.021, 2013.
 [5]. Tippo T., Thanachayanont C., Muthitamongkol P., Junin C., Hietschold M., Thanachayanont A., *The effects of solvents on the properties of ultra-thin poly (methyl methacrylate) films prepared by spin coating*, Thin Solid Films, vol. 546, p. 180-184, doi: 10.1016/j.tsf.2013.05.022, 2013.
 [6]. Mohajerani E., Farajollahi F., Mahzoon R., Bagheri S., *Morphological and thickness analysis for PMMA spin coated films*, J. Optoelectron. Adv. Mater., vol. 9, no. 12, p. 3901-3906, 2007.
 [7]. Syamala Rao M. G., et al., *ZrHfO₂-PMMA hybrid dielectric layers for high-performance all solution-processed In₂O₃-based TFTs*, Mater. Res. Bull., vol. 150, no. December 2021, doi: 10.1016/j.materresbull.2022.111768, 2022.
 [8]. Emanuela E., Herbei V., Musat V., Oertel S., Jank M., *High-k dielectric inorganic-organic hybrid thin films for field effect transistors (FETFT)*, p. 64-68, 2013.
 [9]. Schröder S., Strunskus T., Ababii N., Lupan O., Magariu N., Faupel F., *New vapor deposited dielectric polymer thin films for electronic applications*, p. 94-96, doi: 10.52326/ic-ecco.2021/el.02, 2022.
 [10]. Forte M. A., Silva R. M., Tavares C. J., Silva R. F. E., *Is poly(Methyl methacrylate) (PMMA) a suitable substrate for ALD?: A review*, Polymers, vol. 13, no. 8, doi: 10.3390/polym13081346, 2021.
 [11]. Buchheit R., Kuttich B., González-García L., Kraus T., *Hybrid Dielectric Films of Inkjet-Printable Core-Shell Nanoparticles*, Advanced Materials, vol. 33, no. 41, doi: 10.1002/adma.202103087, 2021.
 [12]. Sathish S., Shekar B. C., *Dip and spin coated nanoscale transparent PMMA thin films for field effect thin film transistors*



and optoelectronic devices, J. Optoelectron. Adv. Mater., vol. 15, no. 3-4, p. 139-144, 2013.

[13]. **Morales-Acosta M. D., Quevedo-Lopez M. A., Alshareef H. N., Gnade B., Ramirez-Bon R.**, *Dielectric properties of PMMA-SiO₂ hybrid films*, Mater. Sci. Forum, vol. 644, no. March, p. 25-28, doi: 10.4028/www.scientific.net/MSF.644.25, 2010.

[14]. **Herbei E. E., Busila M., Alexandru P., Epure S., Musat V.**, *Dielectric Behaviour of PVP 360 and PVA for Thin Flexible Transistors Application*, Mater. Plast., vol. 59, no. 1, p. 1-7, doi: 10.37358/MP.22.1.5554, 2022.

[15]. **Pantano M. F., Pavlou C., Pastore Carbone M. G., Galiotis C., Pugno N. M., Speranza G.**, *Highly Deformable, Ultrathin Large-Area Poly(methyl methacrylate) Films*, ACS Omega, vol. 6, no. 12, p. 8308-8312, doi: 10.1021/acsomega.1c00016, 2021.

[16]. **Aras G., Orhan E., Selçuk A. B., Ocak S. B., Ertuğrul M.**, *Dielectric Properties of Al/Poly (methyl methacrylate) (PMMA)/p-Si Structures at Temperatures Below 300 K*, Procedia - Soc. Behav. Sci., vol. 195, p. 1740-1745, doi: 10.1016/j.sbspro.2015.06.295, 2015.