THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI.
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N^0. 2 – 2013, ISSN 1453 – 083X

HIGH-K DIELECTRIC INORGANIC-ORGANIC HYBRID THIN FILMS FOR FIELD EFFECT TRANSISTORS (FETFT)

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ABSTRACT

The paper discusses the challenges to develop thin films transistors for flexible transparent electronics, displays etc. The sol-gel preparation of hybrid thin films based on dielectric oxides nanoparticles (SiO_2 NPs, ZrO_2 NPs) and polymethy methacrylate (PMMA) is presented. The high-k hybrid thin films, evaluated as gate dielectric in a MIM structures, were deposed by spin-coating teqhnique. The multi-layers (thin films) configuration of MIM structures were investigated by scanning electron microscopy (SEM) and electrical properties. The I-V and C-V curves showed a better dielectric behavior of hybrid films with respect to the simple PMMA films. Dielectric constant values of 2.1, 3.4 and 5.4 have been obtained for PMMA, ZrO_2-PMMA and SiO_2-PMMA films, respectively.

KEYWORDS: hybrid dielectric materials, thin film transistors, morphology, I-V and C-V measurements

1. Introduction

Hybrid materials are a very interesting class of materials that combines the benefits of both inorganic and organic components. [1]. The sol-gel method is the most convenient and suitable method to get the coupling between organic and inorganic phases at the interface level [2-3]. Some of the advantages of this method include low temperature processing as well as high control in the final organic to inorganic phase composition. These advantages are of special interest in the fabrication of flexible electronic devices where the processing temperature is limited by the low processing temperature tolerated by the substrate. In hybrid systems, the poly(methyl methacrylate) (PMMA) organic component provides large area substrate compatibility and flexibility at low processing temperature, while oxide nanoparticles as SiO_2 and ZrO_2 increase the dielectric characteristics of resulting hybrids.

SiO_2-PMMA is one of the most intensively studied hybrid systems in the recent years. Highly transparent SiO_2- PMMA films with different organic - inorganic molar ratios obtained by sol-gel process were reported [4-5]. The properties of the SiO_2-PMMA films such as hardness, refraction index, etc. can be tuned by choosing the appropriated initial compositions of the precursors. There are two principal different routes to introduce inorganic particles into organics. One method is to incorporate inorganic domains into polymer matrices using the sol-gel method. In addition, the polymer may stay contaminated by unreacted educts or byproducts of the precipitation reaction. Another method was blending of preformed inorganic particles into the organic medium. In contrast to the former route, this method is more compatible with the needs of an industrial production [6, 7].

The replacement of rigid substrates with flexible polymeric ones requires novel dielectrics, semiconductors and contacts materials with good mechanical flexibility, low processing temperatures and acceptable performance. As mentioned before, for flexible electronics, PMMA has been assessed as an option for the gate dielectric due to its high resistivity, chemical resistance, thermal stability, mechanical flexibility, low cost and high dielectric constant similar to SiO_2 [8].

One of the most promising high-k dielectric for widespread application is zirconium oxide (ZrO_2), used as gate dielectric. Zirconia is a stable metal oxide with a high dielectric constant (15–25) [9] and a large band gap (5.8eV). It has been reported that ZrO_2 has the lowest leakage current [10]. Moreover, it is a promising material for the fabrication of large-area flexible displays because ZrO_2 films can be transparent and have good adhesion with plastic substrates [11, 13]. These properties have prompted further studies of ZrO_2-PMMA as an alternate gate dielectric material. The understanding of the electrical behavior presents a challenge for any alternative gate dielectric candidate.

The paper presents a study on the electrical properties of SiO_2-PMMA and ZrO_2-PMMA dielectric thin films deposited using a modified sol–gel route. The resulting hybrid thin films were evaluated as gate dielectric using MIM structures. Electrical properties of the hybrid system were studied using current–voltage (I–V) and capacitance–voltage (C–V) data, at 1 MHz frequency.

2. Experimental details

2.1. Film preparation

ZrO_2 (<50nm) and SiO_2 (5nm) nanoparticles used for the preparation of hybrid films were purchased from Sigma Aldrich and PMMA (495kw) from MICRO CHEM. SiO_2-PMMA and ZrO_2-PMMA films were prepared from solutions of 1:1 and 4:1 molar ratios, for both systems. The solution was spin coated for 20 seconds in air, onto the n-doped Si substrates covered with a layer of 100 nm tantalum. The as-deposed films were thermally treated on hot plate at 120^{o}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^{o}C. Finally, metallic aluminum contacts for the capacitor were thermally evaporated through a shadow mask with different areas (180, 320 and 680μm diameters) resulting a multi-layer structure (Figure 1a).

2.2. Film characterization

The thickness of the films was measured from SEM cross-section images obtained with a Zeiss SEM-Raith 150 equipment operated at 10 kV. Aluminum contacts (300nm) were thermally evaporated through a shadow mask on spin-coated hybrid dielectric film.

The I-V and C-V curves were measured in a Metal-Insulator-Metal (MIM) structure (Fig. 1a), using an Agilent 4156 Precision Semiconductor Parameter Analyzer and an HP 4277A Parameter Analyzer, respectively, at 1MHz. Figure 1a depicts a schematic representation of the MIM gate structure used for I-V and C-V measurements, and figure 1b shows a top view optical image of the investigated structure.

The dielectric constant (k) value was calculated from the measured capacitance (C), based on the equation (1):

$$C = \frac{k \cdot \varepsilon_0 \cdot A}{d} \qquad (1)$$

where ε_0 is the permittivity of free spaces, d is the dielectric thickness, C ***is the*** capacitance (F), k is the dielectric constant and A is the capacitor area [12].

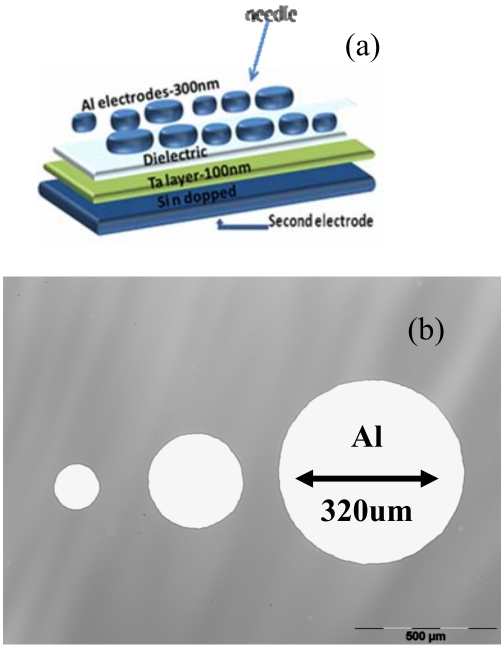
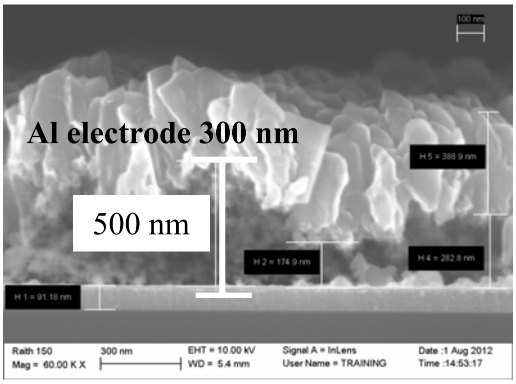


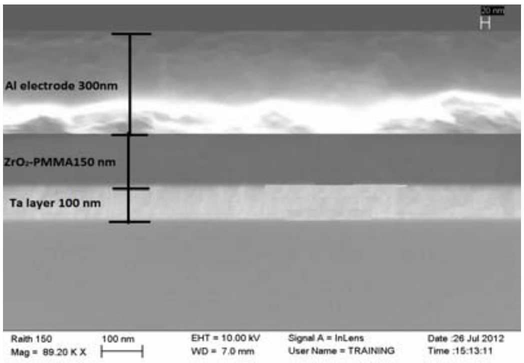
Fig. 1. *Schematic representation of MIM structures (a) and top-view image of the obtained MIM devices (b)*

3. Results and discussion

Fig. 2 show the SEM images of obtained hybrid films with 1:1 and 4:1 molar ratio between oxide nanoparticles and PMMA. For ZrO_2-PMMA, SEM images shows a relatively homogeneous dispersion of nano particle aggregates, the spaces between them being filled by polymer matrix (Fig. 2d-e), resulting in the formation of cross-linked organic - inorganic phases of hybrid films. The thickness of the dielectric layer, is about 150 nm (Fig. 2b). The hybrid films containing silica nanoparticles have a much higher roughness than zirconia films, their thickness varying between 200-600 nm (Fig. 2a). The thickness of the layer of hybrids is increasing by adding nanoparticles, as we saw from the top view of film with PMMA, whose thickness is 70nm (Fig. 2c). For silica films the spaces between agglomerates are bigger than hybrids containing zirconia (Fig. 2f-g). We believe this is due to particle agglomeration because of a weak dispersion in the reaction medium.



a.



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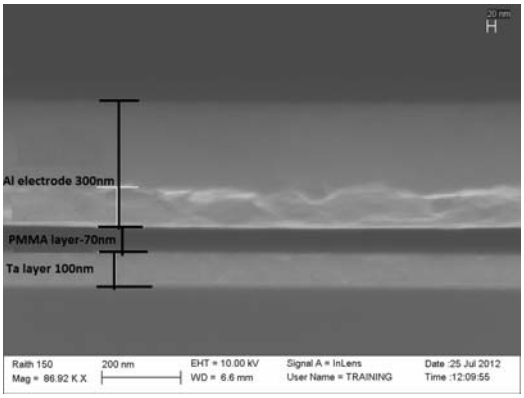
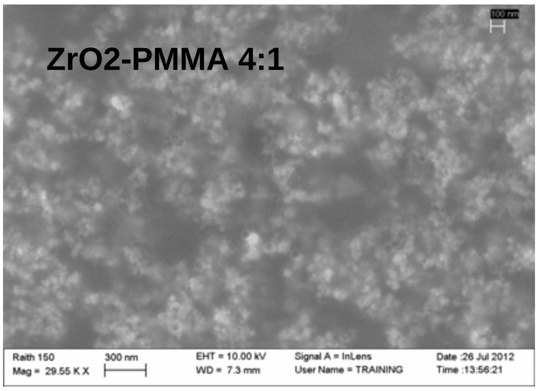
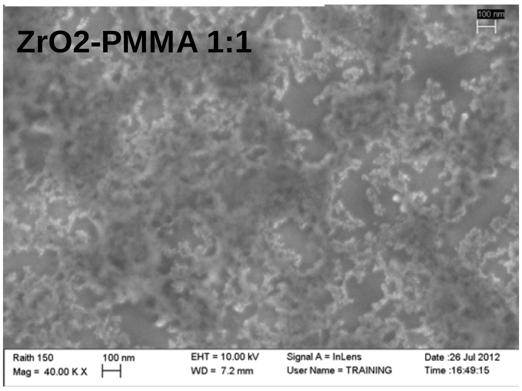


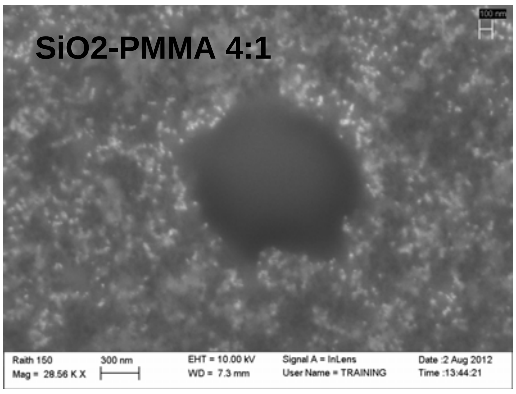
c.



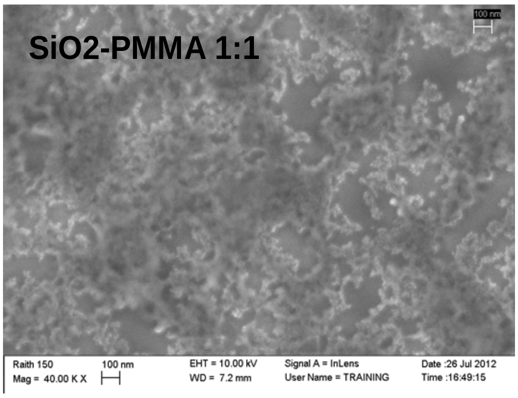
d.



e.



f.



g.

Fig.2. *Cross section SiO_2-PMMA (a), ZrO_2-PMMA (b), PMMA (c) and top views SEM micrographs of hybrid thin films ZrO_2-PMMA 4:1 (d), ZrO_2-PMMA 1:1 (e), SiO_2-PMMA 4:1 (f), SiO_2-PMMA 1:1 (g)*

From the C–V curves (Figs. 3 and 4), were calculated the values of dielectric constant measured at 1MHz frequency in the voltage range ±1 volts for silica hybrid and ± 4 volts for zirconia hybrid. The dielectric constant of devices is summarized in *Table 1.*

Table 1. *Electric parameters of films*

Sample	Capacitance	Thickness, d	Dielectric constant
	[F]	[nm]	[k]
PMMA	$5.39*10^{-11}$	70	2.1
SiO_2-PMMA	$3.5*10^{-10}$	300	3.4
ZrO_2-PMMA	$4.7*10^{-10}$	200	5.4

From *Table 1*, one can observe that the addition of oxide nanoparticles increases the dielectric constant of PMMA. Relevant growth of dielectric constant values is observed in films containing zirconia nanoparticles.

The increment of the capacitance values depends on the ability of existing carriers (holes in this case for n-type substrate) to follow the variation of the applied signal. It is well known that the dielectric permittivity of a material is proportional to its electronic polarization.

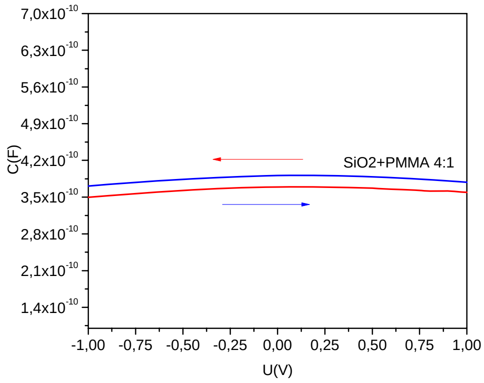


Fig.3. *C-V curve for SiO_2-PMMA thin film*

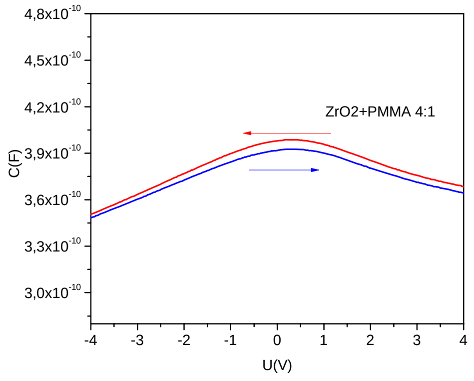


Fig.4. *C-V curve for ZrO_2-PMMA thin film*

Materials with polar groups (i.e. C=O) have large dielectric constants due to the orientation of their electrical dipoles in an applied electric field. Among the organic functional groups, –OH has the highest molar polarization [14].

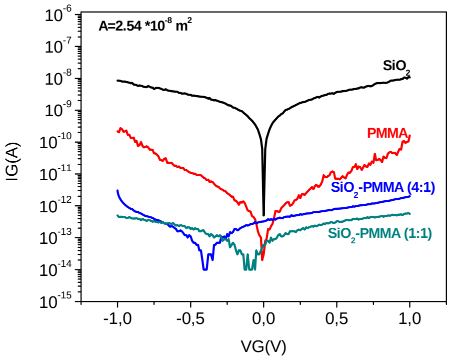


Fig. 5. *I-V curves for SiO_2, PMMA and SiO_2-PMMA thin film different molar ratio*

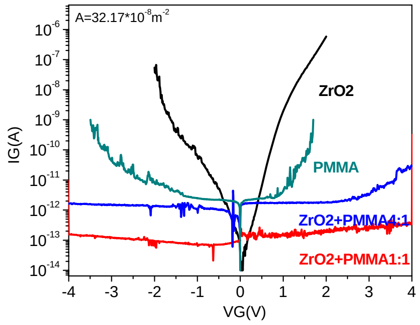


Fig. 6. *I-V curves for ZrO_2, PMMA and ZrO_2-PMMA thin film at different molar ratio*

Polar polymers have a tendency to retain moisture, which further increases their dielectric constants. Also, it is known that for materials with a large number of carbon atoms the polarity increases in the order of single, double and triple chemical bonds, due to enlarged mobility of the *p*-type electrons [15]. The total polarization is the result of the contribution of different factors: type of chemical bond (electronic, atomic or ionic) and polarization responses, at least one of these polarization modes exhibited in dielectric materials. At high frequencies the electronic responses dominate, while ionic contribution is important at low frequencies.

The I-V curves of silica films (Fig. 5) show a dielectric behavior with low leakage current values: 10^{-12} to 10^{-6} A at ±1 volts. By mixing the PMMA with the inorganic SiO_2, the values of the current decreases, being the lowest for the sample with higher inorganic content. The sample with 4:1 molar ratios has a lower leakage current than the sample with 1:1 molar ratio. For zirconia hybrid films, the voltage breakdown increases up to ±15 V (not presented here) with the increase of molar ratio of inorganic/organic content at 4:1 compound. In the same time, the leakage current (Fig. 6) decreases from 10^{-12} A to 10^{-13} when the molar ratio increases at 4:1.

Conclusions

Hybrid SiO_2-PMMA and ZrO_2-PMMA films used as dielectrics in MIM stacks were prepared.

From Capacitance-Voltage electrical data, an increase of dielectric constant of the PMMA films was observed by dopping with silica and zirconia nanoparticles; 3.4 for SiO_2-PMMA and 5.4 for ZrO_2-PMMA hybrid films, respectively.

The I-V curves show a dielectric behavior with values for the leakage current between 10^{-14} and to 10^{-11} A for silica-based hybrid films and 10^{-14}-10^{-12} A for zirconia-based hybrid films. SiO_2-PMMA and ZrO_2-PMMA inorganic-organic films offer attractive opportunities for flexible electronic applications, due to the combined functional features of both organic and inorganic components in a single material.

Acknowledgements

This work was supported by the projects FP7-POINTS (Printable Organic Inorganic Transparent Semiconductor Devices) No. 263042/2011 and CAPACITATI M-III EU 156/2011-POINTS.

The work of Elena-Emanuela Valcu was supported by Project SOP HRD – TOP ACADEMIC 78622.

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