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HYBRID NANOSTRUCTURES BASED OF Ta_2O_5-PMMA FOR ELECTRONIC APPLICATIONS

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ABSTRACT

The scientific interest on hybrid materials is mainly related to understanding the types of interactions between inorganic and organic component and the effect of these interactions on the properties of the new material formed. Hybrid nanostructured materials and especially dielectrics are used for electronics (for gate layer) and especially those applicable in structure of different types of thin film transistors (TFTs).

In this paper is presented the research on thin film hybrid materials based on tantalum oxide (Ta_2O_5) starting with inorganic precursor - tantalum ethoxide and polymethylmethacrylate (PMMA). The chemical method sol-gel involves the precursor-tantalum ethoxide which is hydrolysed and functionalized (with special siloxane compound), and the organic methyl methacrylate monomer. The chemical reactions take place at low temperature below 160 °C. The sol is deposited as thin films by spin-coating to analyse intensity-voltage (I-V) and capacitance-voltage curves (C-V) to determine the electric properties. Metal-Insulator-Metal (MIM) structures were made-up for electric characterisation. The value of leakage currents was between 10^{-10} - 10^{-7} A at ± 40 V. The hybrid films were analysed by scanning electron microscopy (SEM) for thickness and morphology and for thermal stability the sol was investigated by TG and DSC.

The dielectric permittivity ranges between 3.5 and 4 at 1 MHz, depending on the tantalum alkoxide: MMA molar ratio, showing good behaviour for gate layer in future TFTs.

KEYWORDS: hybrid materials; spin-coating; tantalum oxide; PMMA

1. Introduction

The demand for new materials or materials with new properties is currently high. Hybrid materials have been developed to meet certain new performance requirements.

Inorganic-organic hybrids can be utilized in various fields of materials chemistry due to their simple processing and molecular design capabilities. One of the most used method is sol-gel. Currently, there are four major topics in the synthesis of inorganic–organic materials: (a) their molecular engineering, (b) their nanometer and micrometer-sized organization, (c) the transition from functional to multifunctional hybrids, and (d) their combination with bioactive components [1].

The purpose of these materials is to generate desirable properties and functionalities by combining both organic and inorganic components. The aim is to enhance or highlight beneficial traits while simultaneously minimizing or eliminating negative properties or effects. The process involves mixing a polymer with a metal alkoxide and then undergoing hydrolysis and condensation reactions, which are followed by gelification. The composition, processing, and physical properties of materials obtained by this method can vary significantly [2].

In order to use as a dielectric layer in TFTs and OTFT structure, the main requiremnts for materials as organic and inorganic species has to have a small number of charge traps, good processability, reproducibility and stability against degradation, small leakage current and high breakdown potential.

There are a lot of oxide nanoparticles that are considered promotors for dielectric properties such as SiO_2, ZrO_2, Ta_2O_5, HfO_2, etc [3-5].

The thermal and mechanical stability of PMMA, as well as its high resistivity, suitable dielectric constant, and thin film capability, make it an excellent choice [6].

Molas et al. used hafnium aluminium oxide as high k material for dielectric layer in electronic devices as non-volatile memories. They obtained very low current 10^{-7} to 10^{-14} A/cm^2 at an electric field ranges from 0 to -10 MV/cm [7]. Adjusting the zirconium alkoxide concentration in organosiloxane embedded in poly(4-vinylphenol) (PVP) determine the obtaining of dielectric layer for TFTs with higher on/off current ratio, and lower threshold voltage [8]. Based on the sol-gel reaction of SiO_2 and ZrO_2 nanoparticles in PMMA matrix were obtained thin layes for gate dielectrics. The 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 [9]. Thermal silicon dioxide (SiO_2, 100 nm) was used as gate insulator [10] and ITO Sourse/Drain electrode (100 nm) was deposited using reactive sputter.

This work reports details of the preparation of hybrid materials based on tantalum ethoxide embedded in PMMA and presents also the chemical reactions that took place to obtain the sol for thin film. Here we investigated the electrical behaviour of thin films based on Ta_2O_5-PMMA.

2. Experimental

Reagents. Tantalum ethoxide, Ta(OEt)5, precursor (99.9%) was obtained from Cambridge Multivalent Ltd. (Cambridge, UK), Methylmethacrylate reagent grade 99% (MMA)-Sigma Aldrich, Ethanol 95%,were used without other processing steps.

Preparation of sols and thin films. Sols based on molecular precursors were obtained by mixing the metallic alkoxide of tantalum in an alcohol solution and the metallic oxide was generated in situ using tantalum ethoxide as a molecular precursor. For polymer was used the molecular monomer methylmethacrylate which was polymerised after the chemical reaction with the alkoxide (at a temperature and in UV light). For the production of Ta (Oet) 5-PMMA hybrid soil, tantalum ethoxide 99.99% (low Cl) was used. Hybrid films based on Ta_2O_5-PMMA were prepared in two molar ratios 1:1 and 6:1. The solutions were prepared by magnetically stirred at room temperature. First the solution was deposited on a glass substrate to have one and two layers of hybrid layers with 100-150 nm thickness. The deposition was done by spin-coating method at 2000 rpm for 30 seconds.

Thin films characterization. The thermogravimetric analysis-TGA and differential scanning calorimetry-DSC curves were registered in synthetic air (5.0 purity) at 5 K/min. heating rate, using Q 5000IR and Q20, respectively.

The prepared sols, deposited by spin-coating were investigated by scanning electron microscopy (SEM) using a JEOL JSM-7500F/FA microscope from Peabody, MA, JOEL Ltd. USA by top view and in cross section to determine the thickness of the layer.

For electrical characterization, were deposited by thermal evaporation, aluminium contacts (~100 nm in thickness) with different areas to have metal–insulator–metal (MIM). The structure of MIM was presented in an older work of author [3, 5, 9] The intensity–voltage (I-V), capacitance–voltage (C-V), were measured using an Agilent 4156 and HP 4277A Analysers, at 1 MHz, from Agilent Technologies.

3. Results and discussion

Chemical reactions. In the first step the precursor $Ta(OEt)_5$ and the siloxane agent are hydrolysed by the solvent and $Ta(OH)_5$ and $Si(OH)_2$ instable compounds are formed and immediately are condensed and form a complex compound with covalent bonds(-(Ta-O-Si)n-). The monomer reacts with the free chain from the siloxane agent and form new covalent bond as in Figure 1.

Thermal Analysis. The thermal decomposition of the as-prepared sols with different precursors ratios and corresponding aged sols, was done from room temperature-RT up to 600 °C, shown in Figure 2, was investigated for the optimization of the treatment of the as-deposed gel thin films. The TGA and DSC of the soil is presented for the molar concentration 1:1 and was carried out in air of purity 5.0 and with a heating speed of 5 K/min. The components were analysed in individual, binary and ternary systems to observe the points at which they modify certain properties. The data from the thermo-gravimetric analysis were analysed using the TA Analysis software and are presented in Figure 2 a(TGA) and b (DSC).

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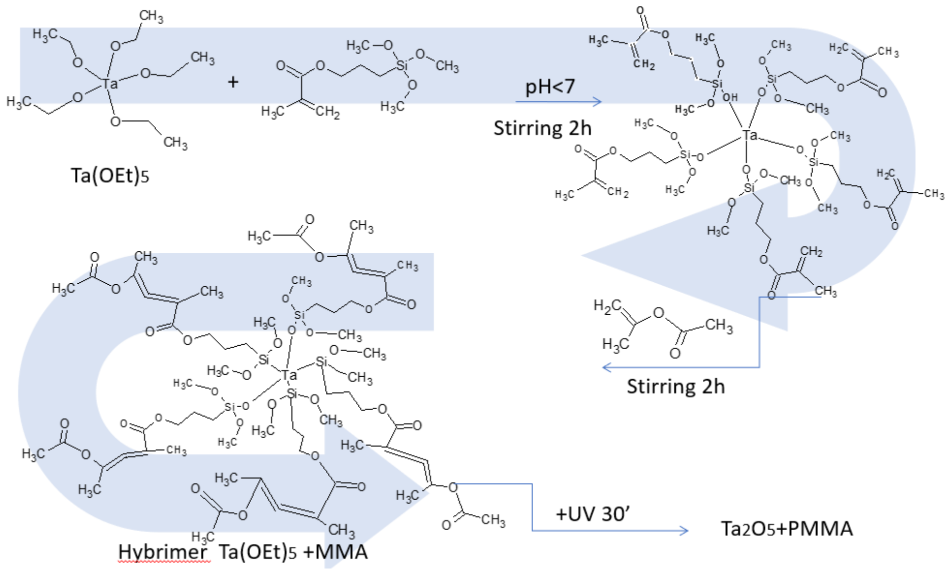

***Fig. 1.** Chemical reactions by sol-gel method*

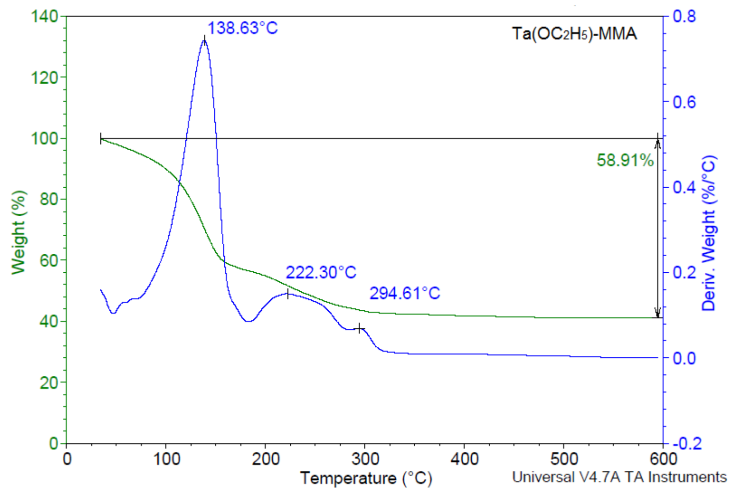

***Fig. 2a.** TGA-DTG of Ta(OEt)$_4$:PMMA*

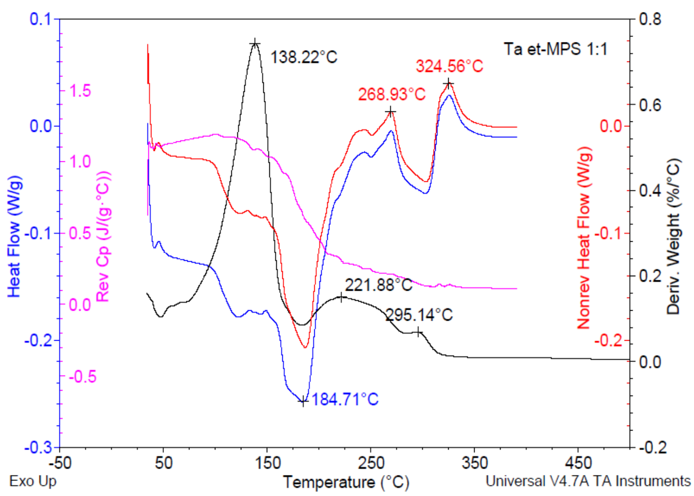

***Fig. 2b.** DSC of Ta(OEt)$_4$:PMMA*

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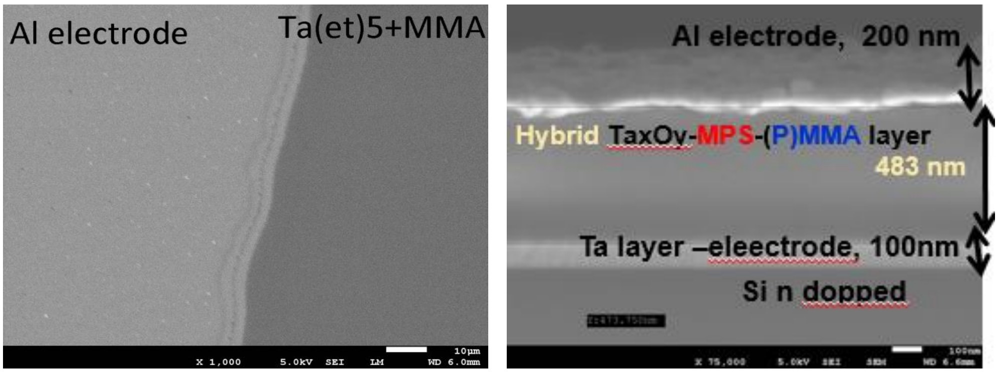
The tantalum ethoxide has two stages of decomposition with the maximum speed at 218 and 280 °C, the siloxane agent has the maximum decomposition speed at 143 °C, the MMA monomer shows a volatile behavior starting at room temperature up to 90 °C, while the PMMA shows the maximum decomposition at 106 °C, the decomposition ending at 125 °C. The thermal decomposition of the two-component system Ta $(OEt)_5$-MPS 1:1, shown in Figure 2a. The temperature for the tantalum ethoxide precursor is higher in the binary system than for individual systems. This leads us to the idea that in the binary system, new links were formed between the alkoxide precursor and the Si-O-Ta covalent bonding agent, bonds that are much stronger and breaking at higher temperatures.

From Figure 2b, we observe an endothermic peak at 187 °C and two exothermic peaks due to crystallization occurring between 270 and 330 °C. The temperature difference between the TG and DSC analysis is attributed to the type of crucible in which the analysis takes place. For TGA was used a crucible made of open Pt, and for the analysis DSC was used coated aluminium crucible.

SEM analysis. The SEM images (Figure 3) on both films display uniform morphology without phase separation between the organic and inorganic components. The very smooth interface between the Ta layer and the hybrid film, but the more irregular interface between the hybrid film and Al electrode can be observed, the latter reproducing the surface roughness of the hybrid polymer.



a b

Fig. 3. *Top view(a) and cross sections (b) SEM images of $Ta(OEt)_5$: PMMA 1:1 hybrid thin films*

Electrical properties of thin films. The I-V curves show leakage current densities of 10^{-10} to 10^{-7} A at electrical field strengths of 0.3 MV/cm and a constant capacitance in the bias range of ±40 V. There are some areas on the top of the sample where the electrode was breakdown, due to the pressing needle.

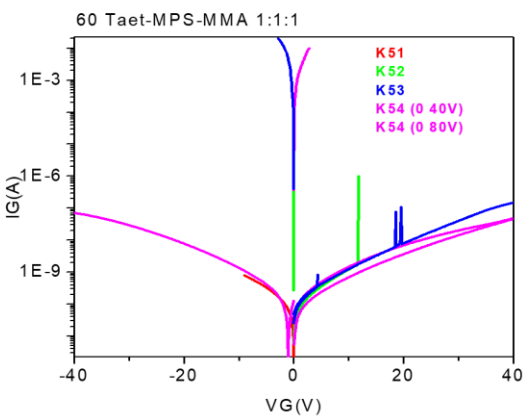


Fig. 4. *I-V characteristics for PMMA layer*

The C–V curves of the investigated films are presented in Fig. 5. The permittivity of the hybrid films were determined from C–V measurements at 1 MHz to be 3.5 for the 1:1 molar ratio of $Ta(OEt)_5$:MMA. The values were determined in the voltage range from -40 to +40 V, at 1 MHz. The dielectric permittivity of a material is proportional to its electronic polarization.

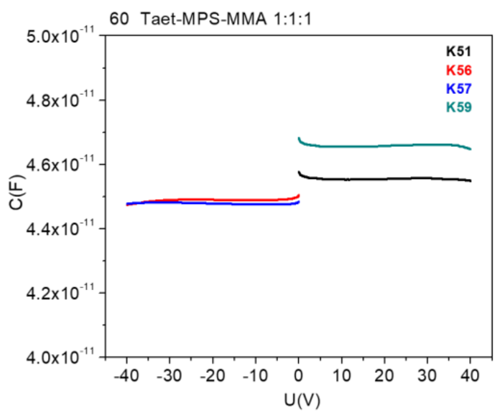


Fig. 5. *C-V characteristics for PMMA layer*

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.

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	$\varepsilon_{r\,m}$
	Position 1	**Position 2**	**Position 3**		
2.054 (K1)	41.23	39.04	44.65	3	3.5
8.043 (K2)	2.135	2.765	1.904	3.7	
32.17 (K3)	4.312	4.657	4.281	3.3	
128.7 (K4)	0.1949	1.3435	0.3971	4	

4. Conclusions

The preparation of $Ta(OEt)_5$:PMMA hybrid dielectric thin films for transparent and flexible electronics was successfully done using sol-gel methods at 160 °C. Hybrid homogenous films that contain Ta_2O_5 and PMMA were made to function as dielectrics for MIM stacks with thickness around 400 nm. From CV electrical data, was determined the permittivity if thin layer between 3 and 4 at1MHz. The values for the leakage current are between 10^{-10} and to 10^{-7} A. The results measured lead us that we can use tantalum oxide in polymer matrix for electronic devices as thin film transistors with flexible and transparent properties.

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