

In situ formation of tantalum oxide – PMMA hybrid dielectric thin films for transparent electronic application

Elena Emanuela Valcu (Herbei)¹, Viorica Musat^{1*}, Susanne Oertel², Michael P.M. Jank², Timothy Leedham³

¹Centre of Nanostructures and Functional Materials-CNMF, Department of Materials Science and Engineering, Faculty of Engineering, "Dunărea de Jos" University of Galați, 111 Domnească Street, Galați 800201, Romania

²Fraunhofer Institute for Integrated Systems and Device Technology IISB, Erlangen, Germany

³Multivalent Ltd., Eriswell, Suffolk IP27 9BJ, United Kingdom

*Corresponding author. Tel: (+40) 757070613; E-mail: viorica.musat@ugal.ro

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ABSTRACT

Solution-processed high-k dielectric hybrid thin films prepared at temperatures below 200°C represent a subject of increasing scientific interest satisfying current requirements for printable thin film transistors used in transparent flexible electronics. In this work, we propose a new approach for the synthesis of new tantalum oxide-PMMA hybrid dielectric thin films at 160°C by modified sol-gel method, using as precursors tantalum ethoxide cluster ($\text{Ta}(\text{OC}_2\text{H}_5)_5$) and methyl methacrylate monomer (MMA). So far it has not been reported *in situ* formation of tantalum oxide nanocrystals in hybrid dielectric materials at this low temperature. Hybrid sols with 1:1 and 4:1 ($\text{Ta}(\text{OC}_2\text{H}_5)_5$):MMA molar ratios were used for spin-coating of thin films. The thermal behavior of these sols was observed in order to optimize the post-deposition treatment of the films. The hybrid films were investigated by scanning electron microscopy (SEM) for thickness and morphology, by grazing incidence x-ray diffraction (GIXRD) and high resolution transmission electron microscopy (HRTEM) for tantalum oxide phase formation. TaO_2 single crystals with a diameter of about 2 nm embedded in an amorphous phase were identified. The dielectric properties of the hybrid thin films were derived from the characterization of Metal-Insulator-Metal (MIM) structures by current-voltage and capacitance-voltage measurements. *I-V* curves show a leakage current between 10^{-12} and 10^{-7} A and a constant capacitance in bias range ± 50 V. For films with 1:1 and 4:1 molar ratio, the leakage current density ranges between 10^{-9} - 10^{-3} A/cm² and 10^{-9} - 10^{-4} A/cm², and the limit of the current density goes to an electric field of ± 1.2 MV/cm and ± 2.5 MV/cm, respectively. In the case of films with 1:1 molar ratio, the applied voltage was up to 70 V in positive domain and no breakdown was observed for the dielectric layer. These results show higher current density for a larger voltage range, than the characteristics leakage current values reported for PMMA (10^{-8} A/cm²) at 0.3 MV/cm. The value of the permittivity ranges between 3.5 and 7.5 at 1 MHz, depending on the tantalum alkoxyde: MMA molar ratio, suggesting very promising future of these hybrid dielectric thin films for the fabrication of transparent TFTs, which can serve for next generation of transparent and flexible electronic devices. Copyright © 2015 VBRI Press.

Keywords: Tantalum ethoxide cluster; modified sol-gel; hybrid thin films; TaO_2 nanocrystals; dielectric constant.



V. Musat obtained PhD in physical chemistry from University of Bucharest, Romania and presently is working as Full Professor in the Department of Material Science, University "Dunărea de Jos" of Galați (UDJG), Romania. Her research area is focused on chemical preparation of metal oxide and metal oxide-based hybrid nanomaterials for application in transparent electronics, optoelectronics, sensors, photocatalytic and antimicrobial fields. She is working on transparent and conductive oxide (TCO) thin films, dielectric materials, semiconductive oxide nanoparticles and 1D nanostructures, nanoporous oxide and SiO_2 -based nanocomposite thin films, micro/meso-porous thin films, magnetic oxide nanoparticles and related sintered materials and ferrofluids. She is director of Centre of Nanostructures and Functional Materials (CNMF-

UDJG) and member of more national and international scientific societies.



E.E. Valcu (Herbei) received PhD from University "Dunarea de Jos" of Galati, Romania in 2014. His area of research is focused on hybrid materials and nanomaterials application in transparent electronics. She has worked on studies for dielectric nanoparticles obtained from organometallic precursors for application in electronics.



S. Oertel, Research Scientist, received her PhD in chemistry (Inorganic Materials) from University of Erlangen-Nuremberg in 2004, since 2008 she is with Fraunhofer IISB working on synthesis and characterization of inorganic nanoparticles. Since 2010 she is active in the field of inorganic precursors for solution-processed metal oxide TFTs and device fabrication as well as ink formulation of different functional material for inorganic printed electronics.

Introduction

The development in the last decade of flexible transparent electronics requires low temperature deposition methods of different functional thin films. High-k dielectric thin films prepared at temperature below 200°C to be used as dielectric gates for printable thin film transistors is a subject of increasing scientific interest [1-4]. To this end, the advantages of the hybrid materials that combine the properties of both organic polymer (flexibility, elasticity, adherence to substrate, facile and low temperature processing) and inorganic compounds (thermal, electric, optical properties, chemical and mechanical resistance) [5] can be used to develop high-k dielectric thin films. Since the hybrid materials derive from an intimate combination, often mediated by the formation of a chemical bond, of inorganic and organic building blocks, it may show a consistent increase of the properties and functionality, since the resulting material not only combines the typical features of both, organic and inorganic ones, but can also present additional/enhanced properties deriving from the interaction of both [6].

The dielectric features of an organic polymer can be merged with those of a metal oxide to produce new hybrid dielectric thin (<1 μm thick) and ultrathin (<100 nm thick) films for the development of thin films transistors and capacitors [8]. Taking the advantages of organic polymers, the hybrid dielectric materials are particularly attractive because they can be easily synthesized and processed at low temperature and low cost. Due to the interest in using hybrid materials as active layers for transparent and flexible devices and optoelectronics applications [5-9], there is an increase of studies on their preparation and properties measurements [7]. For the use of flexible electronics in large-surface applications, printing has been proposed as a viable solution. Many experiments have been made toward creating printable TFTs. Fully printed TFTs for applications such as radio-frequency identification, D flip-flop have been successfully demonstrated using a combination of roll-to-roll and inverse gravure printing [9].

TaO₂, Ta₂O₅, ZrO₂ and HfO₂ transition metals oxides that were recently demonstrated as promise for high-k dielectric materials in submicron range technology [2, 10] are potentially very important inorganic compounds for obtaining hybrid high-k thin films. TaO₂ and Ta₂O₅ thin films have high static dielectric constant and good insulating properties [11] and can be used for capacitor and gate materials inside of metal-insulator-metal structures. Combining tantalum oxide and PMMA dielectric polymer with very good processability and adhesion to different substrates, *Myoung et al.* obtained hybrid bi-layered dielectric nanocomposite thin films for transparent

electronic devices. In this paper we propose the preparation of homogeneous hybrid films starting from tantalum oxocluster (i.e. aggregates of metal atoms linked by oxygen bridges) precursor and a polymerisable organic monomer groups, as methylmethacrylate, generating a building blocks covalently connected hybrid network [20]. This approach provides an efficient route to embed an alkoxide or an oxocluster into a polymer network thus obtaining molecularly homogeneous materials in which the inorganic oxoclusters are covalently linked to the organic backbone [12,13]. The sol-gel route using metal-alkoxide precursors as source for the inorganic component is very suitable to prepare homogeneous hybrid materials because it offers low-temperature synthesis and, by varying the molar ratio between the inorganic and organic components, the dielectric properties of resulting films can be tuned [10]. The mutual distribution and interactions at the organic/inorganic interfaces affect the final properties of the materials. This method was used for the preparation of hybrid SiO₂-PMMA [3-4]. The literature presents a very small number of papers about the synthesis of hybrid materials based on tantalum alkoxide precursors [11-13]. *Pickup et al.* reported sol-gel preparation of hybrid xerogel with optical properties based on reaction between tantalum alkoxide (Ta(OEt)₅) and tetra ethyl orthosilicate TEOS [16]. *Basch et al.* discuss on the preparation of hybrid materials with good thermo mechanical properties using [(Ta₄O₂OEt)₈(OMc)₄] oxocluster and methylmethacrylate [17]. *S. Gross et al.* presents dielectric characterization of the inorganic-organic hybrid film based on zirconium oxocluster-crosslinked PMMA. They obtained a dielectric constant of 1.93 at 1 kHz and 25°C, that indicates this material as a promising dielectric thin film [6]. *S.Bennabi et al* obtained in situ polymerization of organic-inorganic compounds, using maghnite-H + as a green solid catalyst. They used a high variety of metal ions clusters, i.e. inorganic nodal points, interconnected by organic ligands to generate rigid and oriented metal-oxygen-carbon (M-O-C) bridges [12, 25].

There are no reports in literature on the in situ preparation of hybrid tantalum oxide nanocrystals-PMMA thin films by sol-gel method. The objective of our research is the development of a class of hybrid metal oxide-PMMA- based thin films using metal alkoxides and MMA precursor and tuning the dielectric characteristics of the prepared hybrid films by tailoring the nanocrystal size of the dielectric metal oxide, for applications in transparent thin films transistors for the transparent electronics. Our strategy for obtaining efficient dielectric films, at temperatures below 200 °C, was to simultaneously combine the precursors for both components, organic and inorganic, for the in situ generation of a very homogeneous, at nanoscale, hybrid material with strong chemical bonds between the two components. In this paper, we report the fabrication of efficient dielectric thin films, in MIM structures, through the generation of tantalum oxide nanocrystals embedded in a thin amorphous matrix of dielectric polymer. The novelty of this work consists of obtaining nanocrystals of tantalum oxide species directly by condensation reaction inside of a polymerisable matrix of MMA monomer. The synthesis of new hybrid thin films containing tantalum oxide nanocrystals took place at 160°C

by modified sol-gel route in which a 3-trimethoxysilylpropyl methacrylate (MPS) coupling agent is used to have a good interaction between the tantalum oxide nanocluster and methylmethacrylate monomer.

The electrical measurements were developed to see the current behavior in the thin films and to understand the electrical properties of these materials. The capacitance measurements showed a good dielectric constant for the 4:1 molar ratio. So far as author's knowledge is concerned, this article may be the first report on a thorough study on the dielectric properties and morphological structure on the hybrid Tantalum oxide-PMMA sols and films. The objective of the present paper is to optimize the molar ratio between tantalum ethoxide and methyl methacrylate in order to ensure the adherence, flexibility and good dielectric properties of the films.

Experimental

Materials

Tantalum ethoxide 99.9999% (metals) was purchased from Multivalent Laboratory, 3-trimethoxysilylpropyl methacrylate 98% (MPS), methylmethacrylate contains ≤ 30 ppm MEHQ as inhibitor, 99% (MMA) and absolute ethanol 99.99% (Et-OH) purchased from Sigma-Aldrich were used as received without further purification for the preparation of hybrid films.

Preparation of sols and thin films

For the sol preparation, 5g of tantalum ethoxide was dissolved into absolute ethanol at room temperature under magnetic stirring. After the solution becomes clear, the MPS coupling agent and the methyl methacrylate monomer were successively added under continuous stirring. The pH of the solution was kept under 4. The molar ratios between reagents are presented in **Table 1**. The sols were aged at 50 °C until became transparent and provide good viscosity for the film deposition.

Table 1. Investigated samples.

Symbol	Type of sample	Composition	Molar ratio	Post-deposition treatment
S1	Sol	Ta(OEt) ₅ :MPS	1:1	As prepared
S2	Sol	Ta(OEt) ₅ :MPS:MMA	1:1:1	As prepared
S3	Sol	Ta(OEt) ₅ :MPS:MMA	1:1:1	T and UV
S4	Sol	Ta(OEt) ₅ :MPS:MMA	1:1:1	UV
S5	Thin film	Ta(OEt) ₅ :MPS:MMA	1:1:1	T and UV
S6	Thin film	Ta(OEt) ₅ :MPS:MMA	4:1:1	T and UV

For the dielectric film deposition, two sol compositions corresponding to tantalum ethoxide: MMA molar ratios of 1:1 and 4:1 were prepared (**Table 1**). The resulting homogeneous solution was spin-coated onto cleaned *n*-doped silicon substrates, covered by sputtering with a 100 nm thick tantalum layer (first electrode). The post-deposition treatment of films consisted in 10 minutes hot plate thermal treatment at 160°C (noted "T" in **Table 1**) and exposed at UV radiation ($\lambda=254$ nm) emitted by an H 466.1 UV lamp (noted "UV" in **Table 1**). For electrical characterization, aluminum as second electrode (~200 nm in thick) with different areas was evaporated through a shadow mask on top of the hybrid dielectric film.

Sols and thin films characterization

The individual reagents and different sols (S1-S4 in **Table 1**) prepared for the hybrid film deposition were characterised by Fourier transform infrared (FTIR) spectroscopy. The FTIR spectra were recorded using a JASCO 6200 FTIR Spectrometer.

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

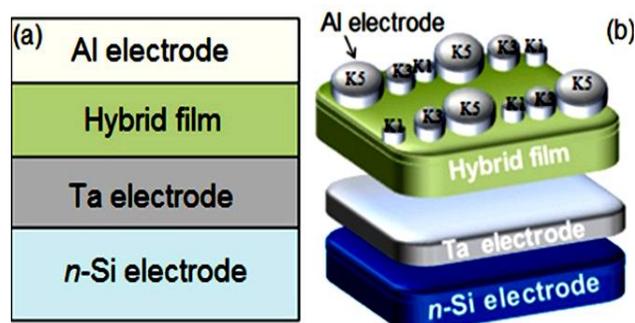


Fig. 1. Schematic representation (a and b) of MIM structure used for the measurement of I-V and C-V characteristics of thin films.

Results and discussion

Structural characterization

Fig. 2 shows the FTIR spectra of the individual reagents, Ta(OEt)₅:MPS (S1) two-component sol and Ta(OEt)₅:MPS:MMA (S2-S4) three-component sols submitted to similar treatment as the film post-deposition treatment (see **Table 1**), in order to investigate the structural transformations that take place. In these spectra, absorption bands that appear in several domains, corresponding to different components, can be observed [**17-19, 22**].

The strongest absorption bands between 750-950 **Fig. 2(b)** and 1000-1150 **cm⁻¹ (Fig. 2(c))** are associated mainly with the inorganic (Si-O-Si, Si-OH) and inorganic-organic components (Ta-O-C, Si-O-Si and Si-O-C), respectively.

The vibration bands attributed to Si-O-C and C-O-C can be observed at 1110 **cm⁻¹** and 1145 **cm⁻¹**, respectively;

- Peaks of Ta-O-Ta below at 650 cm^{-1} (**Fig. 2(a)**), Ta-O-C at ~900 cm^{-1} and 1000-1100 cm^{-1} (around 1072 cm^{-1}) (**Fig. 2(a)**) and Ta-O-Si around 800 cm^{-1} [**16**] can be considered for the hybrid sols;

-The wide band centered at 3350 cm^{-1} (**Fig. 2(d)**) is attributed to O-H stretching modes [**17**] and Si-OH and Ta-OH unreacted groups.

The condensation of MPS coupling agent resulted in higher intensity of the vibration bands of Si-O-Si bridges at ~ 880 cm^{-1} and lower intensity of the vibrational peak at 940 cm^{-1} related to the unreacted Si-OH groups [**17**]; this confirm that the condensation of Si-OH groups from MPS took place during heat-treatment.

The Ta-O-Si bands are assumed to be between 960 and 1080 cm^{-1} [17], but in **Fig. 2(b)** a shift at around 800 cm^{-1} due to the presence of the PMMA matrix is observed.

Comparing the FTIR spectra of the samples S1, S2 and S4 (**Fig. 2 (a-d)**), one can notice many similarities, that means that the UV treatment (30 minutes) does not have a significant influence on formation of the inorganic (Ta-O-Ta and Si-O-Si or Ta-O-Si) structure, but has promoted the polymerization of the C=C bond, that can be observed in the spectrum of MMA raw material (**Fig. 2(a)**). One can notice the disappearance of the C=C band in the spectra of the UV treated samples, as a result of the polymerization of the organic monomer in the resulted hybrid structure.

The MPS coupling agent and MMA monomer have almost the same structure (C=C and COO⁻ bonds) leading to overlapping bond vibrations. The wide band centered at about 1100 cm^{-1} is the result of an overlapping bands effect of the Si-O (1060 cm^{-1}), Si-O-C (1130 cm^{-1}) and C-O-C (1200 cm^{-1}) bands. This demonstrates the tantalum bonding formation in the hybrid samples (S1-S4) as result of different treatment (160°C heating and/or UV). The difference is clearly observed for sample S3, in which the thermal treatment was applied before UV irradiation, and can be assumed as a condensation process between hydrolyzed Ta-OH groups, Si-OH groups and between each-other groups occurs first (before polymerization) and favors the formation of Ta-O-Ta, Si-O-Si and Ta-O-Si bridges, respectively.

The presence of the Ta-O-Si bands in samples heated at 160°C together with the disappearance of C=C peak confirm that the condensation and polymerization reactions successfully led to the formation of homogeneous material at molecular level (sample S3 in **Fig. 2(b)**). The presence of Ta-O-Ta bands in FTIR spectra of sample S3 heated at 160°C suggests the formation of tantalum oxide nanocrystallites in the hybrid material.

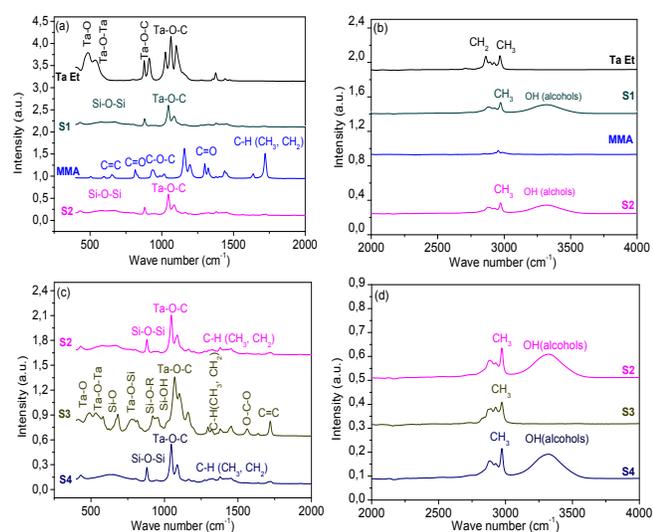


Fig. 2. FTIR spectra of individual components and hybrid sols, in 400-2000 cm^{-1} (a, c) and 2000-4000 cm^{-1} (b, d) spectra ranges.

SEM characterization

Fig. 3 shows the cross-section SEM images of the hybrid films with 1:1 **Fig. 3(a)** and 4:1 **Fig. 3(b)** molar ratio between Ta-alkoxide and MMA precursors. 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 alkoxide precursor provides higher sol viscosity. For both films, the SEM images show homogeneous morphology without phase separation between the organic and inorganic components. Very smooth interface between the Ta layer and the hybrid film, but more irregular interface between the hybrid film and Al electrode can be observed, the latter reproducing the surface roughness of the hybrid polymer.

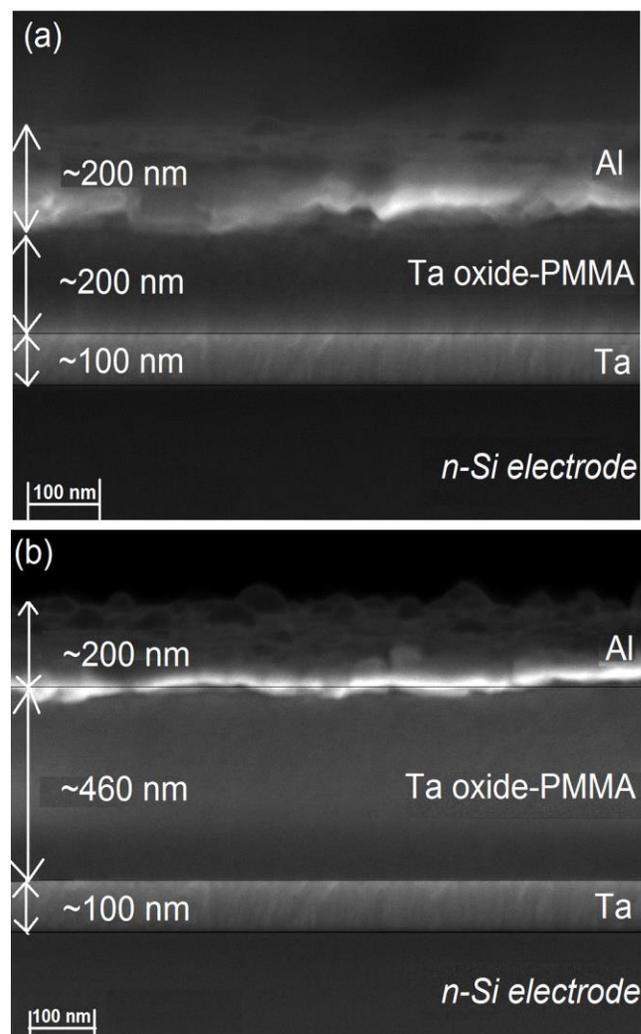


Fig. 3. Cross sections SEM images of Ta(OEt)₅:MPS:PMMA 1:1:1 (Sample S5) (a), Ta(OEt)₅:MPS:PMMA 4:1:1 (Sample S6) and (b) hybrid thin films.

TEM characterization

The atomic resolution TEM images (**Fig. 4**) offers details about the structure at molecular scale of the hybrid film obtained after thermal treatment at 160°C followed by exposure to UV radiation. One can notice *in situ* formation of nanocrystallites with average diameter ranging from 1.9 to 2.1 nm embedded at molecular scale in an amorphous phase. By measuring the interplanar distances for the larger nanocrystallites, the (110) Miller indices orientation of TaO₂ crystalline phase with interplanar distance of 2.65 Å was identified. The inset highlights the short-range order structure of individual Ta atoms. The formation of tantalum

oxide nanocrystallites by polycondensation of hydrolyzed tantalum ethoxide cluster and by polymerization of MMA during UV radiation result in the generation of new homogeneous hybrid material.

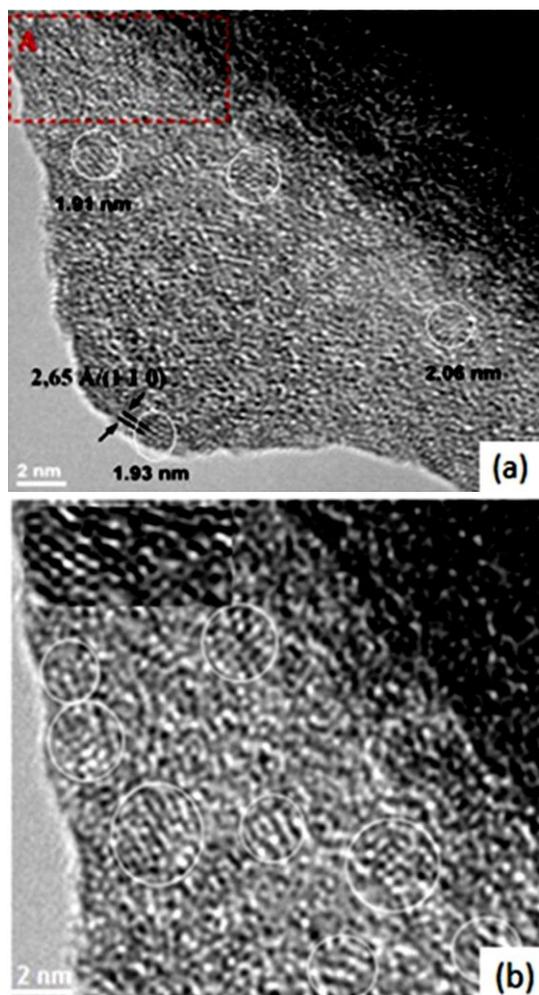


Fig. 4. High resolution TEM image (a) and detail from A zone (b) of hybrid film (4:1), thermal treated at 160°C and exposed at UV radiation (Sample S6).

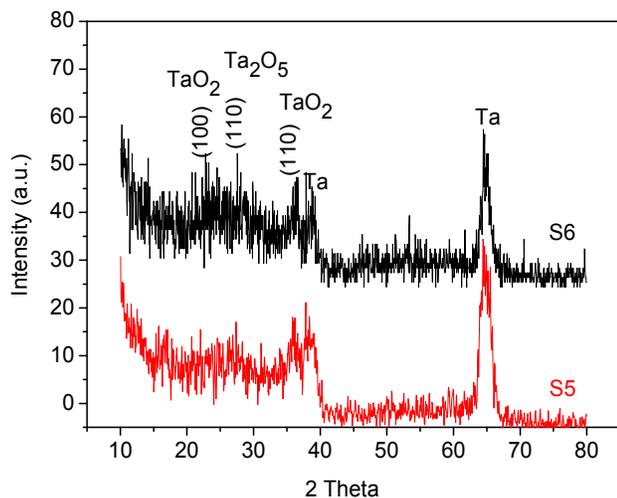


Fig. 5. Grazing incidence XRD patterns of (4:1) (S6) and (6:1) 4:1 (S5) molar ratio hybrid film, thermal treated at 160°C and exposed at UV radiation.

The HR-TEM results are consistent with the grazing incidence XRD patterns (GIXRD) (**Fig. 5**) that confirm the formation of cubic TaO₂ phase (ASTM00-019-1296) [20]. In **Fig. 5**, the first two most important peaks of the TaO₂ cubic phase, (110) and (100), can be seen. Using Scherrer's formula, average crystallite diameter (for TaO₂) of 1.89 nm was calculated in the (4:1) hybrid film treated at 160°C and then exposed at UV radiation (Sample S6). In the GIXRD patterns shown in **Fig. 5**, one can also notice low intensity (110) diffraction peak of Ta₂O₅ phase [20].

In the literature are reported several chemical composites based on tantalum oxide such as TaO_{2-x}, TaO₂, Ta₂O_{5-x} and Ta₂O₅ that can be formed depending on the deposition methods and parameters [10, 20-21]. For the insulating Ta₂O_{5-x} (mixed valence Ta₂O₅-TaO₂ compounds) phase, the bandgap ranges from 4 eV to 5 eV depending on the chemical compositions based on tantalum oxides [9]. The band structure calculations showed that the TaO and TaO_{2-x} phases are metallic, whereas the TaO₂ and Ta₂O₅ phase is insulator. TaO₂ and Ta₂O₅ phases can be mixed in the nonconductive α -Ta₂O_{5-x} phase [10, 20, 21].

Electrical measurements

The electrical properties of tantalum oxides ranges from metallic conductor (TaO_{2-x}) to insulator (TaO₂, Ta₂O_{5-x} and Ti₂O₅), depending on the oxidation degree; not only Ta₂O₅, but also TaO₂ was demonstrated with good dielectric properties for high-*k* gate application [18, 20].

Fig. 6 (a) shows the I-V characteristics of the investigated films for gate voltages from -50 V to +50 V. The leakage current density taken at an electric field of 0.3 MV/cm is typically in the range of 5·10⁻⁸ in the case of 1:1 molar ratio (S5) and 10⁻⁶ A/cm² in the case of 4:1 molar ratio (S6).

With respect to reference values reported for pure PMMA dielectric (10⁻⁸ A/cm² @ 0.3 MV/cm) [23] the current density is slightly increased for the sample with low inorganic content and significantly increased for the sample with higher Ta/Ta oxide load. Though the current increases steadily, no hard breakdown can be detected up to at least ±1.2 MV/cm in the case of low Ta(OEt)₅ content and about ±2.5MV/cm in case of high inorganic content (not shown). In the 1:1 case, one sample exhibited an electrical breakdown at a voltage as high as 70 V (respectively 3.5 MV/cm) in the positive domain, i.e. injection of electrons from the Ta bottom electrode.

The moderately increased leakage currents could be explained by the presence of C=O groups and residual (unreacted) O-H groups of MPS or tantalum ethoxide in the hybrid films. The decrease of the unreacted hydroxyl groups concentration to decrease the leakage current is especially for dielectrics with higher inorganic/linker content a key point to obtain Ta(OEt)₅:MPS:PMMA hybrid films applicable as high-quality dielectric gate in electronic devices. Further studies are considered to correlate the dielectric behavior of films with the effect of temperature and duration of post-deposition thermal treatment.

The C-V curves of the investigated films are presented in **Fig. 6(b)**. The permittivities of the hybrid films were determined from C-V measurements at 1 MHz to be 4 for the 1:1 and 7.5 for the 4:1 molar ratio of Ta(OEt)₅:MMA.

The good dielectric behaviour of the hybrid films can be attributed to the presence of TaO₂ and Ta₂O₅ nanocrystalline phases mixed in to an nonconductive α -Ta₂O_{5-x} phase. These results are in agreement with the results reported by M.J. Lee *et al* for insulating Ta₂O_{5-x} films [10, 20].

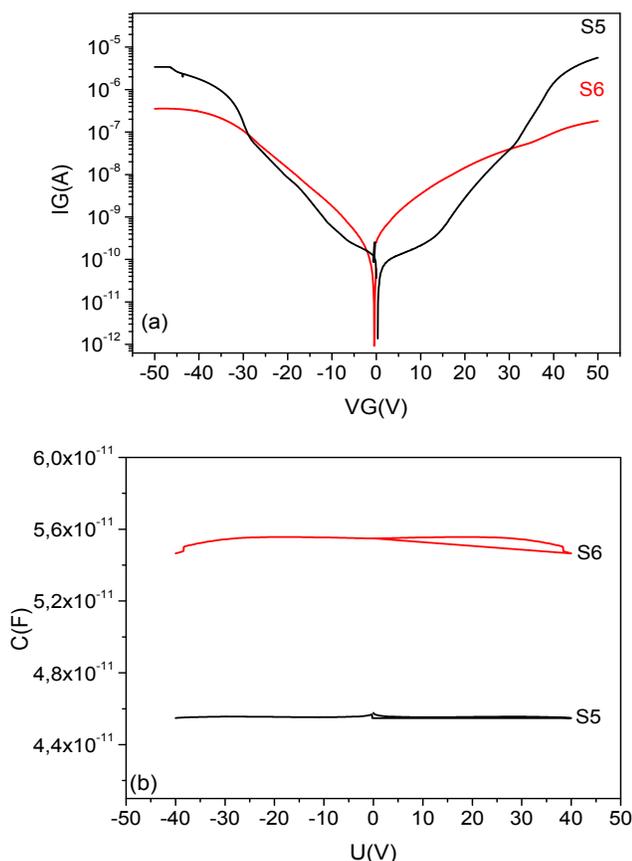


Fig. 6. I-V (a) and C-V and (b) curves for Ta (OEt)₅:MPS:PMMA 1:1:1 (Sample S5) and 4:1:1 (Sample S6).

The dielectric permittivity of a material is proportional to its electronic polarization. Usually, materials with polar groups (i.e. C=O, OH) have large dielectric constants due to the orientation of their electrical dipoles in the electric field. Taking also into consideration that the hydroxyl group has the highest molar polarization [3, 4, 11, 24], it is clear that the permittivity increases when increasing the Ta(OEt)₅:MMA molar ratio.

Conclusion

New Ta-oxide:PMMA hybrid dielectric thin films targeting transparent and flexible electronics were successfully prepared by sol-gel methods at 160 °C. Tantalum dioxide nanocrystallites with an average size of about 2 nm embedded in amorphous matrix were successfully synthesized inside the films with 4:1 Ta-oxide:PMMA molar ratio. So far, has not been reported *in situ* formation of tantalum oxide nanocrystals, more so in hybrid materials, at this low temperature. FTIR spectra confirmed the formation of Ta-O-Ta. GIXRD has revealed the presence of TaO₂ and Ta₂O₅ nanocrystalline phases. HRTEM data confirmed the formation of TaO₂ nanocrystallites. The use of 3-trimetoxypropyl methacrylate (MPS) as coupling agent improves the compatibility between the organic and

inorganic phases, allows obtaining smooth surface homogeneous films without phase separation. The I-V curves show leakage current densities of 10⁻⁸ to 10⁻⁶ A/cm at electrical field strengths of 0.3 MV/cm and a constant capacitance in the bias range of ±50 V. This good dielectric behaviour of the hybrid films was obtained as a result of a synergic effect of the interaction between the two TaO₂ and Ta₂O₅ nanocrystalline phases, merged into a nonconductive α -Ta₂O_{5-x}, and the hybrid amorphous matrix, in which these nanocrystals are dispersed. Dielectric constant of 7.5 was obtained for the hybrid films with 4:1 molar ratio, suggesting very promising future of these hybrid dielectric thin films for the fabrication of transparent TFTs, which can serve for next generation of transparent and flexible electronic devices. The study will be continued to establish the conditions required to prepare stoichiometric nanocrystalline Ta₂O₅ phases embedded into amorphous matrix.

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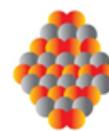
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