Sol-gel Preparation of ZrO_2-PMMA for Thin Films Transistors

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The hybrid metal oxide/polymer thin films are a very promising class of dielectric materials used as a gate for the last generation of field-effect transistors (TTFT). The zirconia nanoparticles are suitable for the formation of discrete inorganic building blocks covalently bonded to the organic polymers in hybrid materials. In this paper, zirconia nanoparticles (ZrO_2 NPs) and polymthylmetacrylate (PMMA) were used to obtain hybrid thin films. The zirconia nanoparticles were functionalized with MPS agents by using a modified sol-gel route. Poly methyl methacrylate was used as an organic component to obtain flexible and resistant hybrid thin films with thickness in nanometer range by using spin coating techniques. This work presents a second work for the optimization of the homogeneity of thin film layer to obtain layer with better dielectric properties. Thin films with good adherence to silicon substrates and dielectric permitivity between 4.5 and 6 have been obtained. The morphology of thin films were investigated by scanning electron microscopy and the dielectric behavior was evaluated based on I-V and C-V measurements.

Keywords: zirconia nanoparticles, PMMA, modified sol-gel, hybrid thin films, dielectric constant

In the past decades, the incorporation of inorganic nanoparticles into polymer matrix received tremendous interests, since it can obviously improve the properties of polymers and/or render polymers with novel functions. Among all these studies, special attentions have been focused on polymethyl methylacrylate (PMMA)-based nanocomposites, because the small size effect of nanoparticles could retain the original transparency of PMMA. Iron oxides [1], Ag [2], TiO_2 [3,4], ZnS:Mn [5], ZnO [6], and $LaPO_4:Ce^{3+}$ [7] nanoparticles have been introduced into PMMA, providing optical, electrical, magnetical, nonlinear optical, luminescent, or UV-blocking properties. Generally, four routes for fabrication of PMMA-based nanocomposites were applied: in-situ generation of nanoparticles in PMMA solution (1), in-situ generation of nanoparticles in methyl methacrylate (MMA) monomer and following radical polymerization (2), blending ex-situ preformed nanoparticles with PMMA solution (3), and in-situ bulk polymerization of MMA/nanoparticles dispersion (4). As for the last ones two processes with preformed inorganic nanoparticles, the big challenge is encountered to assure the homogeneous dispersion of nanoparticles in the nanocomposites. Since the blending method using PMMA solution is confronted with the serious environmental problem due to the organic solvents employed, in-situ polymerization of MMA/nanoparticles dispersion would be more desirable especially for the production of bulk sheets. A lot of surface modifiers have been chemically attached to the nanoparticles to improve the compatibility of nanoparticles with MMA and further PMMA. Successful examples include tert-butylphosphonic acid for ZnO nanoparticles (NPs) [8], octylphosphonic acid for ZrO_2 and TiO_2 nanoparticles [9], stearic acid for calciumcarbonate nanopowder [10], and 3-glycidoxypropyltrimethoxysilane for alumina nanoparticles [11], just to name a few. These ligands, however, are inert in radical polymerization. The surface-treated nanoparticles during polymerization tend to aggregate due to depletion force, reducing the transparency of PMMA-based nanocomposites especially at high nanoparticle load [8, 9]. To overcome this problem, vinyl group-containing ligands were used as alternatives. For instance, g-methacryloxypropyltrimethoxysilane (MPS) was employed for the functionalization of SiO_2 nanoparticles [12] and ZrO_2 nanoparticles [13], and oleic acid for modification of ZnO nanoparticles [14] and NaYF4:Yb^{3+}, Er^{3+}.

The dielectric gate in an OTFT is a critical determinant of its electrical performance. The electrical performance of the transistor is significantly influenced by the charge carrier density accumulated in the semiconductor channel, which is determined by the gate dielectric capacitance. Gate dielectrics for high-performance OTFTs require a uniform smooth surface, low leakage current density, and high dielectric constant (k). For flexible electronics on plastic substrates, solution processable gate dielectrics are preferred due to their easy processability and low-temperature capability.

There are three major types of dielectrics used in OTFTs: inorganic dielectric, polymeric dielectric, and self-assemble layer. For inorganic dielectric materials, silicon dioxide is commonly used as the gate insulator in OTFT. However, this kind of OTFT requires a relatively high voltage (about 100 V) for operation. In order to reduce the operating voltage and so the power consumption, high-k material is often used as a gate dielectric in OTFTs. Several high-k dielectrics have been employed to fabricate OTFT, for example, HfO_2 [15], Al_2O_3 [16], TiO_2 [17], Ta_2O_5 [18], and $BaTiO_3$ [19]. The performance of organic transistors depends largely on the quality of the gate insulator, the insulator/organic interface, the morphology of the organic thin film, and the charge injection process. It is essential to develop a suitable and high-quality gate insulator with appropriate morphology to achieve a smooth insulator/organic interface. The as-deposited high-k films are usually loosely packed and contain impurities and defects such as: oxygen vacancies, oxygen interstitials, and/or oxygen deficiency [20]. These defects and impurities will cause transient charge trapping in the high-k dielectric and

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leakage current [21]. In this study, one of the most promising high-k dielectric for widespread application, zirconium oxide (ZrO_2), is used as the dielectric gate. ZrO_2 is a stable metal oxide with a high dielectric constant (15–25) [22] and a large band gap (5.8 eV). It has been reported that ZrO_2 has the lowest leakage current [23]. Moreover, it is a promising material for the fabrication of large-area flexible displays because the ZrO_2 films can be transparent and have good adhesion with plastic substrates [24]. The effects of ZrO_2 annealing treatment time in nitrogen ambient on the electrical properties of CuPc-based organic thin film transistors are investigated. The electrical and physical characteristics of the devices are presented. In this paper, zirconia nanoparticles (ZrO_2 NPs) and polymthylmetacrylate (PMMA) were used to obtain hybrid thin films with dielectric properties by using a modified sol-gel route.

Experimental part

Films preparation

ZrO_2 (<50nm) nanoparticles dispersion used for the preparation of hybrid films were purchased from Sigma Aldrich and PMMA (495kw) from MICRO CHEM. The zirconia nanoparticles were separated by centrifugation and washed in absolute methanol to remove the water traces. For the functionalization we used 3-trimetoxy-silylpropyl methacrylate 98% (MPS). The nanoparticles were dispersed in absolute tetrrahydrofuran solvent after the washing procedure and the agent was added. The time for functionalization was 24 h. After the functionalzation the nanoparticles were washed in absolute ethanol to eliminate the agent excess. ZrO_2 NPs-PMMA sols were prepared from solutions of 1:1 and 4:1 molar ratios for both systems. The solution was spin coated for 20 s in air, onto n-doped Si substrates covered with a layer of 100 nm tantalum. The as-deposed films were thermally treated on hot plate at 120°C for 30 min. The scheme for obtaining hybrid sols is presented in figure 1. The substrates were cleaned following a standard procedure: washed in water for three times, dipping in isopropanol for 1 minute and cleaning with water, dried with nitrogen stream and hotplate for 5 min at 120°C. Finally, metallic aluminum contacts for the capacitor were thermally evaporated through a shadow mask with different areas (180, 320 and 680 μm diameters) resulting a multi-layer structure (fig. 2a).

Films 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 (300 nm) 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. 2a), using an Agilent 4156 Precision Semiconductor Parameter Analyzer and a HP 4277A Parameter Analyzer, respectively, at 1MHz. Figure 2b depicts a schematic representation of the MIM gate structure, and figure 2c a cross section of structure measured. The dielectric constant (*k*) value was calculated using the measured capacitance (*C*), based on the equation (1);

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

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.

Results and discussions

Figure 3 shows the SEM images of obtained hybrid films with 1:1 and 4:1 molar ratio between oxide nanoparticles and PMMA. For ZrO_2NPs-PMMA, SEM images shows a relatively homogeneous dispersion of nano particle aggregates, the spaces among them, being filled by polymer matrix (fig. 3b-d), resulting in the formation of cross-linked organic - inorganic phases of hybrid films. The thickness of the dielectric layer, is between 120 and 140

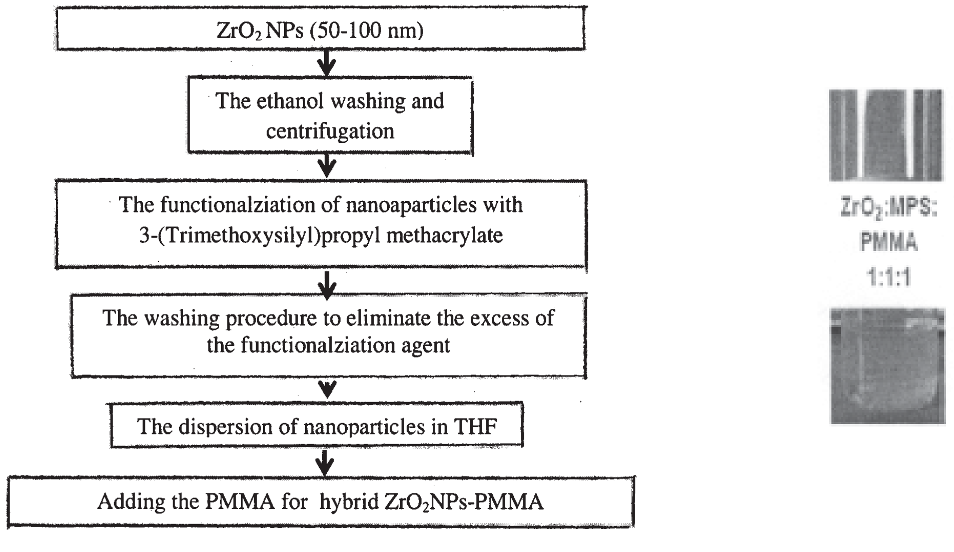

Fig. 1. Schematic representation for the modified sol-gel procedure for obtaining hybrid thin films

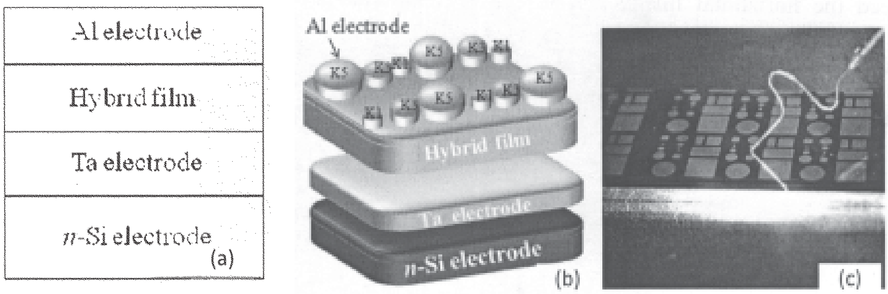

Fig. 2. Schematic representation (a, b) and top view of MIM structure (c) used for the measurement of I-V and C-V characteristics of thin films

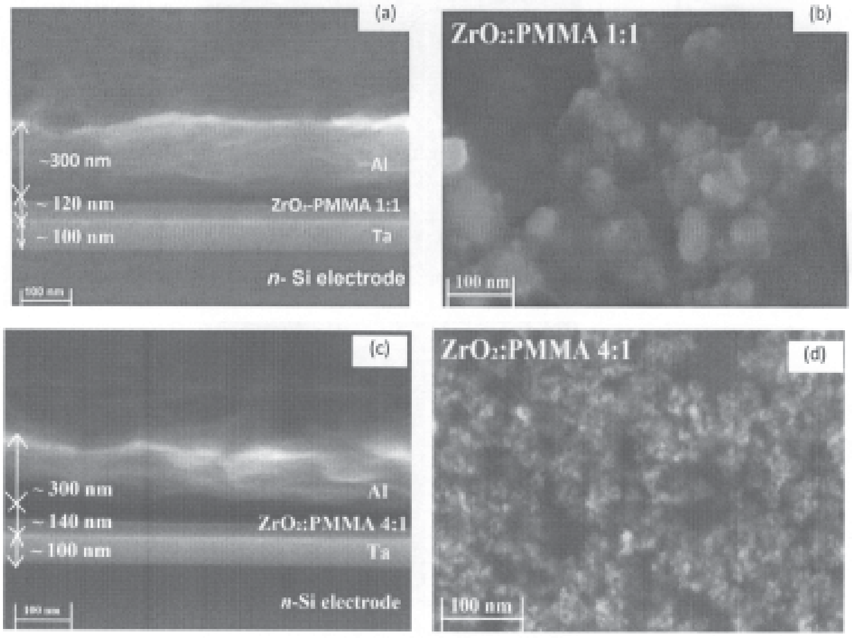

Fig. 3. Cross section and top view SEM images of hybrid thin films: ZrO_2-PMMA 1:1(a, b) and 4:1 (c, d)

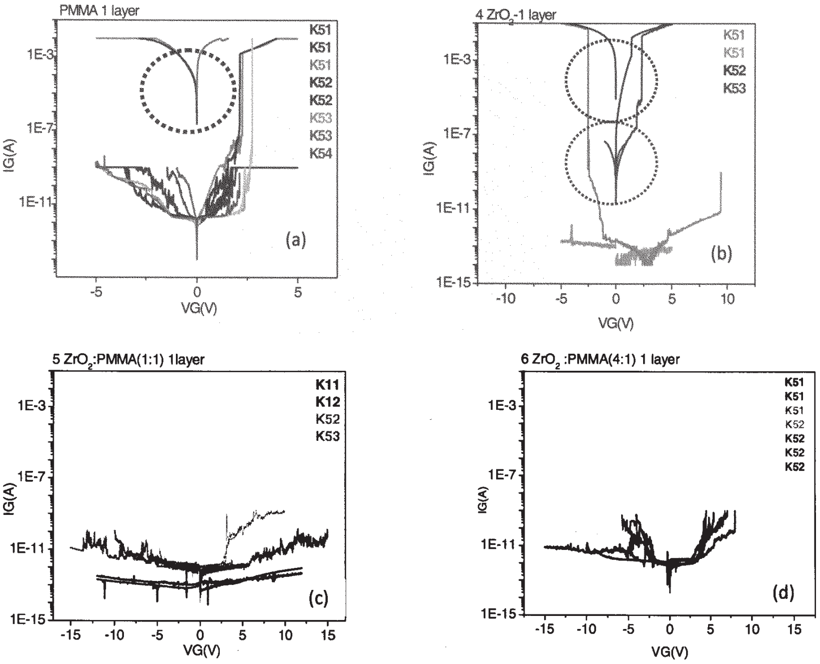

Fig. 4. I-V curves of thin films deposed with 1 layer: PMMA (a), ZrO_2 (b), ZrO_2 : PMMA 1:1 (c), ZrO_2:PMMA 4:1 (d)

nm (fig. 3a-c). The thickness of the 4:1 ZrO_2NPs-PMMA is higher because of the concentration of nanoparticles.

The behaviour in the electric field of thin films based on ZrO_2-PMMA, the I-V curves respectively are presented in figure 4. For comparation, we presented the I-V curves of the samples containing PMMA and ZrO_2 nanoparticles deposed by spin coating in one layer. The I-V curves present different behaviors for the PMMA, ZrO_2 and ZrO_2-PMMA films. For the films containing PMMA the I-V curves show low leakage current in the voltage range of ± 5V. For this sample, the film presents a breakdown of the dielectric layer, which can be attributed to the existence of defects in the sample.

For the zirconia films, the curves present big noises, the breakdown of the dielectric occurs very quickly and it was not possible a measurement of the film for more electrodes. The breakdown occurs at a low voltage (at about 0.1 V). This behavior can occur due to the agglomeration of the nanoparticles that prevent the homogenous deposition of aluminium electrodes and its perfect contact with the dielectric film. Also, the layer presents a different thickness and that is why one can notice different values of the leakage current (Area K53 of fig.4 b). The films were measured taking into consideration a compliance limit (10^{-6}A), so as not to destroy the dielectric layer because we want to measure also for the capacitance behaviour. By adding the PMMA with a lower dielectric constant but high homogenity, the dielectric behavior improves. For the ZrO_2-PMMA hybrid films (fig. 4 b and c), the currents that pass through the dielectric have low values (10^{-14}-10^{-10}A), showing a very good dielectric behaviour. The hybrid films ZrO_2-PMMA, with 1:1 and 4:1 molar ratio, have a better dielectric behaviour than the films with ZrO_2, the leakage are lower and the voltage applied is between -15 and 15V. The I-V measurements on hybrid films present constant behaviour in the measured interval. The curves present lower noises and one can associate that with the presence of polarizable organic molecules when the current passes through the layer. The dielectric constant of ZrO_2:PMMA thin hybrid films with 1:1 and 4:1 molar ratio were calculated from the C-V curves (table 1).

The dielectric constant of the hybrid films is not a summing of the values of PMMA and zirconia constants. For the investigated films, the dielectric constant ranges between 3 and 6.

Table 1
ELECTRIC PARAMETERS OF HYBRID THIN FILMS

Sample	Capacitance (F)	Thickness d (nm)	Dielectric constant (k)
ZrO_2-PMMA 1:1	$1.1 * 10^{-12}$	120	4.63
ZrO_2-PMMA 4:1	$1.3 * 10^{-12}$	140	6.38

Conclusions

Hybrid thin films of ZrO_2NPs:PMMA with 1:1 and 4:1 molar ratio, as a dielectric layer in MIM stacks, were prepared. The I-V curves show dielectric behaviour with leakage current values between 10^{-14}-10^{-12} A.

Values of 4.6 and 6.3 of dielectric constant of ZrO_2NPs:PMMA hybrid films with 1:1 and 4:1 molar ratio, respectively, were calculated from C-V curves. These hybrid films offer attractive opportunities for flexible electronic applications, due to the combined functional features of both organic and inorganic components in a single molecular scale.

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