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Synthesis and characterization of nanohybrid lanthanum oxide doped with polystyrene in electronic devices

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Organic thin-film transistors (OTFTs) obtained from thin gate dielectrics of organic and inorganic hybrids as thin films have very good electrical properties such as high-K dielectric and low leakage current, and are a very remarkable and practical category in physics-chemistry research. In the present work, we synthesized a polystyrene (PS)/La_2O_3 hybrid by the sol-gel method and studied its properties for replacing silicon oxide as a good gate dielectric material for organic field-effect transistor devices. The structure and morphology of PS/La_2O_3 were studied by using X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR).The effects of different temperatures and concentrations on the size of nanocrystallites were also studied by the X-ray powder method. The dielectric constant (K) and capacity(C) were measured using GPS 132 A technique. The obtained results indicated that PS/La_2O_3 nanocomposite prepared with the highest concentration of PS at the lowest temperature has an amorphous structure which can reduce leakage current and tunneling current due to its high EOT (equivalent oxide thickness). It can be used for future OTFT flexible devices.

Keywords: Dielectric, Nanocomposite, Organic Material, PS/La_2O_3, XRD, Transistor.

INTRUDUCTION:

Nowadays, thin film transistors with an active layer of an organic material have attracted much attention due to their process ability, low cost and flexibility [1-2]. Organic gate dielectrics are favored very much because of their solution process ability and flexibility which can lower process temperature, but polymer gate dielectrics have capability to be used in electronic chipsets due to their low K (dielectric constant) and high current densities [3-5]. On the other hand, the dimensions of microelectronic devices are placed in nano scales. The need for smaller and faster devices made nano electronics of high importance in today´s technological world. Use of smaller electronic devices increases processing speed and lowers electricity usage, but this causes problems such as leakage current in Mosfet (metal oxide semiconductor field effect transistor). Correspondingly, one of the solutions is to use nanostructured transistors [6-7]. Organic-inorganic hybrid thin film transistors have good electrical properties such as high dielectric constant, low leakage current density and less than 40 nanometer thickness [8]. We believe that the higher k-gate dielectric materials can be introduced as a better alternative for gate dielectric in future devices [9]. In this case there has been much more literature on organic-inorganic hybrid thin film transistors. Several attempts have been made to get materials with better electrical properties such as PS/TiO_2 [10], PVP/TiO_2 [11], PS/titania [12], PMMA/SiO_2 [13] and this should be continued to get a better hybrid. In this research we tried to synthesize a new PS/La_2O_3 hybrid nanocomposite to get a better structure. Lanthanum oxide nanocrystallite has a lot of attractive properties such as high-k dielectric and energy band gap of 4.3 eV [14]. It has amorphous structure at $\leq$500°C and can reduce leakage current [15]. These properties make it a good choice for use in future electrical devices as gate dielectric [16]. Polystyrene has good resistance against water absorption and excellent thermal and electrical insulation. So PS/La_2O_3 can be used as a good insulator to lower leakage current in electrical devices [17, 18]. In this work, we used sol-gel methods to synthesize PS/La_2O_3 with different density and temperatures and we studied its structural and electrical properties.

EXPERIMENTAL

The materials used were from Merck; the sets used were: XRD (GBC-MMA-007), SEM (Tescan Vega II) and FTIR (Shimadzu).

PS/La_2O_3 nanocrystallites were prepared by a sol-gel procedure with lanthanum chloride as a raw material. We added 5.9 g of lanthanum chloride ($LaCl_3.7H_2O$) to 300 ml of distilled water and put it over magnetic stirring at room temperature. We added

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2.7 g of cetyltrimethylammonium bromide (CTAB) into the above solution at room temperature under stirring till the solution became transparent. Then we put 6.0 ml of ammonia into the solution to reach a pH value of 10. After 2 h, polystyrene solution (0.07 g PS in 2 ml o-xylene) was added to this solution. After vigorous stirring for 24 h, the sol solution was dried at 80 °C for 72 h. Finally, the obtained white solid gel was centrifuged, washed with distilled water and ethanol to remove possible ions remaining in the final product and dried it again at 80 °C. As a result, PS/La_2O_3 powder was obtained. The same procedure was performed with two other PS amounts (0.14, 0.28 g) and we calcined at 300 °C and 500°C. We studied the effect of temperature and concentrations on the sample structure. The crystal phases of the product were investigated by XRD technique; morphological analysis was done by SEM technique. The size of the nanocrystallites was determined by the X-powder method. The dielectric constant (K), and the capacity (C) were measured by GPS 132 A technique.

RESULTS AND DISCUSSION

The structure of the PS/ La_2O_3 nanocrystallites was investigated using XRD analysis. Figures 1,2 show the XRD patterns of the PS/ La_2O_3 as-prepared and annealed at temperature 300 °C and 500 °C with different PS amounts: 0.07, 0.14, 0.28 g .

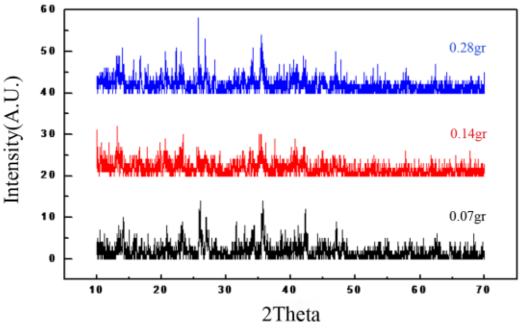


Fig 1. XRD patterns of PS/La_2O_3 nanocrystallites at 300 °C temperature with different PS amounts.

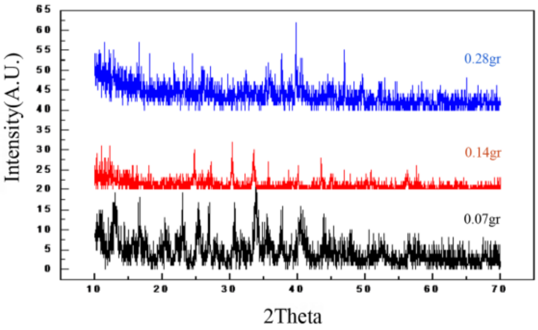
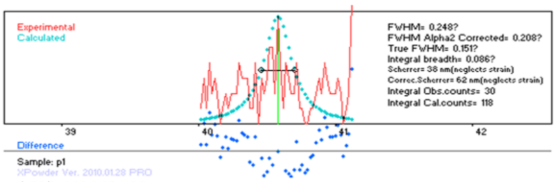
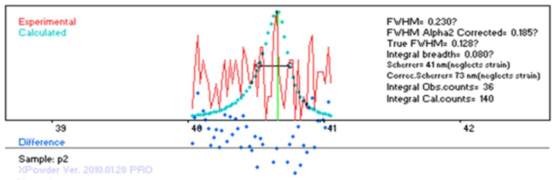


Fig 2. XRD patterns of PS/La_2O_3 nanocrystallites at 500 °C temperature with different PS amounts.

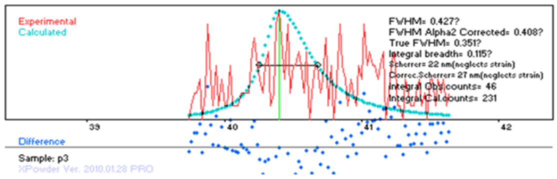
As XRD shows, increasing PS concentration in the PS/La_2O_3 nanocomposite, the peak of PS/ La_2O_3 decreased and the peak width increased. In fact, as the amount of polystyrene increased, it affected the size of nanocrystallites and increasing calcination temperature affected the size and the structure of nano particles. Figure 3 shows the sizes of PS/ La_2O_3 nanocrystallites at 300 °C temperature with different PS concentration.



a) PS/La2O3 0.07gr PS



b) PS/La2O3 0.14gr PS



c) PS/La2O3 0.28gr PS

Fig 3. Peaks of nanocrystallites obtained at 300 °C using X-powder method.

X-powder analysis showed that increasing the amount of polystyrene decreased the size of nanocrystallites of PS/ La_2O_3 and the structure of the sample became more amorphous. Increasing the temperature decreased the size of nanocrystallites of PS/ La_2O_3 and the lower size of the nanoparticles is related to the use of 0.028 g of PS and 300 °C (Table 1).

Table 1. Size of nanocrystallites of PS/La_2O_3 at different temperature

Sample	Calcination temperature T/C	Size of nanocrystallites S/nm
0.07 g PS/La_2O_3	300 ˚C	62 nm
0.14 g PS/La_2O_3	300 ˚C	73 nm
0.28 g PS/La_2O_3	300 ˚C	27 nm
0.07 g PS/La_2O_3	500 ˚C	29 nm
0.14 g PS/La_2O_3	500 ˚C	52 nm
0.28 g PS/La_2O_3	500 ˚C	28 nm
Pure La_2O_3	300 ˚C	51 nm
Pure La_2O_3	500 ˚C	48 nm

The capacitance measurements were conducted with a Gps 132A precision LCR meter. The dielectric constants were calculated according to the following equation:

$$C = K\varepsilon^{\circ}\frac{A}{d}$$

where C is the measured capacitance, ε° is the permittivity of free space, A is the area of the capacitor, and d is the thickness of the dielectric. According to Table 2, the highest K is related to an amount of 0.028 g of PS at 300 °C.

Table 2. Dielectric constants and capacity of PS/La_2O_3 at different temperatures and different PS amounts. The highest K is registered at 300 °C with 0.28 g of PS.

Sample	Calcination temperature T/ C	K	C (nf)
0.07 g PS/La_2O_3	300 ˚C	67.8	0.081F
0.14 g PS/La_2O_3	300 ˚C	34.6	0.016 F
0.28 g PS/La_2O_3	300 ˚C	82.67	0.066 F
0.14 g PS/La_2O_3	500 ˚C	24.7	0.021F
0.28 g PS/La_2O_3	500 ˚C	57.72	0.027 F

Figure 4 shows the Fourier transform infrared spectrum (FTIR) of PS/La_2O_3 obtained at 300 °C with different PS amounts.

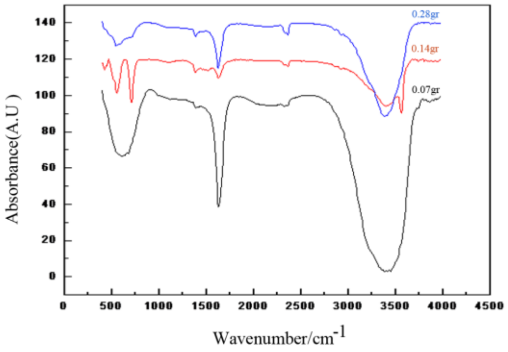


Fig. 4. FTIR spectrum of PS/La_2O_3 at 300 °C temperature with different PS amounts.

The FTIR spectrum in the area of 1650 cm^{-1} shows that the absorption is due to an aromatic ring and the maximum absorption is about O-H hydrogen bond; the peak at wavenumber 2923 cm^{-1} is related to the C-H bond of methylene group and the peak at wavenumber 540-601 cm^{-1} is related to the C-Cl. The FTIR spectrum of the nanocomposite showed that as the concentration and temperature increased, the absorption decreased which results in bonding failure. The morphologies of PS/La_2O_3 hybrid nanocomposites were analyzed using SEM technique (Figures 5, 6, 7).

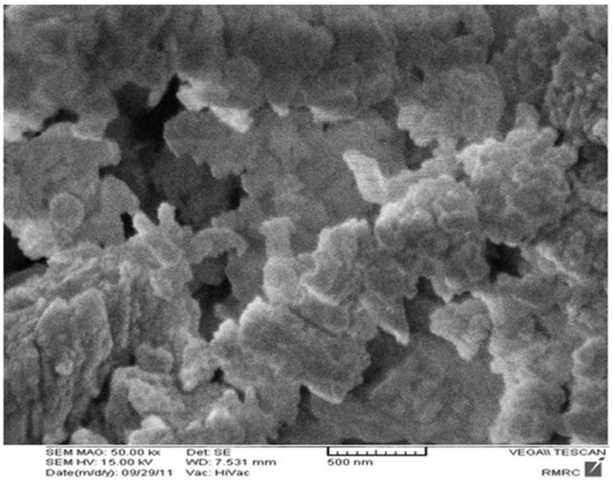


Fig. 5. SEM image of PS/La_2O_3 nanocrystallites obtained at 500 ˚C with 0/07 g PS

The SEM comparison between PS/La_2O_3 and La_2O_3 showed that adding polystyrene to lanthanum oxide changed its structure and made it uniform and the size of the nanocomposite decreased leading to amorphous PS/La_2O_3. As the SEM image of the nanocomposite obtained with 0.28 g of PS at 300 °C shows, it has uniform structure and lower size of nanoparticles that are more amorphous than other PS/La_2O_3 with different concentration and temperature.

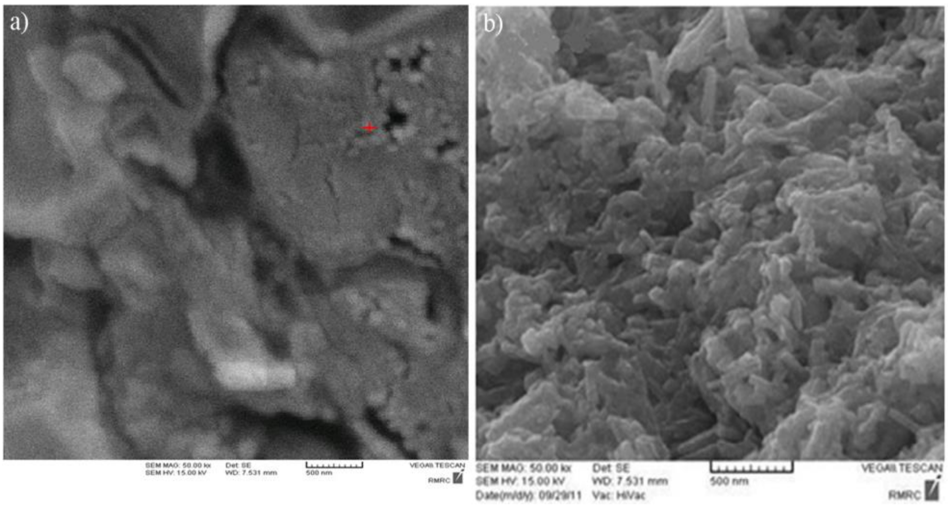


Fig. 6. SEM image of PS/La_2O_3 nanocrystallites obtained: (a) at 300°C with 0.28 g PS (b) SEM image of La_2O_3 at 300°C.

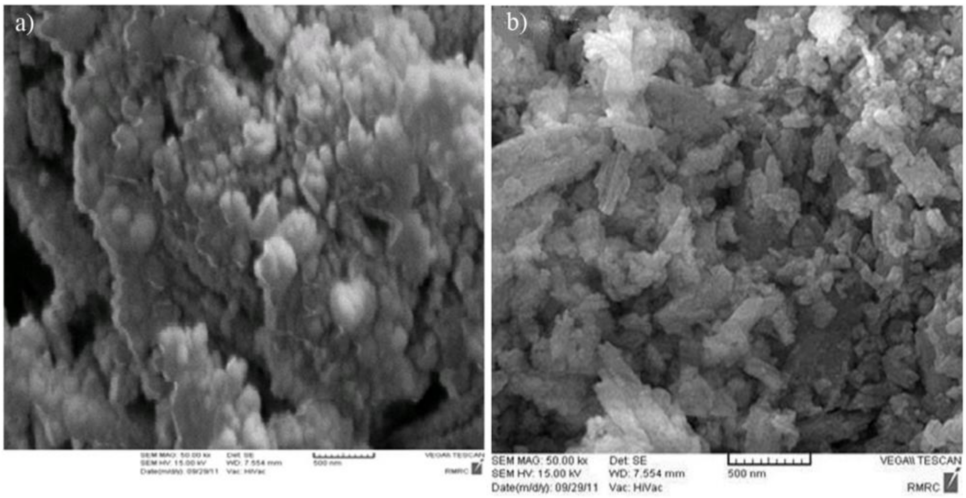


Fig. 7. SEM image of PS/ La_2O_3 nanocrystallites obtained: (a) at 500°C with 0.28 g PS (b) SEM image of La_2O_3 at 500°C.

According to the previous research, La_2O_3 was introduced as a high-K dielectric gate and was used in NVMs [15]. In another study monohybrid TiO_2/PS was investigated and results showed that it can be used as a gate insulator [10]. Conspicuously, the quality of the dielectric surface improved significantly and it reduced the leakage current. According to the above conclusion, we decided to use La_2O_3 instead of TiO_2. The obtained results also showed a very impressive quantity of amorphous phase in the samples and considerably better reduction of leakage current than in previous research.

CONCLUSION

In this work, we studied PS/La_2O_3 with different contents and temperatures using XRD, SEM, FTIR and GPs 132 A techniques. Results showed that the nanocomposite PS/La_2O_3 with 0.28 g of PS at 300 °C is more amorphous, has a higher K- dielectric constant and can be used as a good insulator in electric devices to prevent tunneling leakage current. It can be used in future OTFT flexible devices.

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СИНТЕЗА И ОХАРАКТЕРИЗИРАНЕ НА НАНОХИБРИДЕН ЛАНТАНОВ ОКСИД ДОТИРАН С ПОЛИСТИРЕН ЗА ЕЛЕКТРОННИ УРЕДИ

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(Резюме)

Органични транзистори с тънък филм (OTFTs), получени от тънки диелектрици на органични и неорганични хибриди като тънки слоеве имат много добри електрически свойства като висока диелектрична K и нисък ток на утечка, и са забележително и практическо поле за физико-химични изследвания. В настоящата работа, ние синтезирахме полистирен *(PS) /* La_2O_3 хибриден по метода на зол-гел и изучихме неговите свойства за заместване на силициев оксид като добър диелектричен материал за органични транзисторни устройства. Структурата и морфологията на *(PS) /* La_2O_3 бяха изследвани с помощта на рентгенова дифракция (XRD), сканираща електронна микроскопия (SEM) и инфрачервена спектроскопия с трансформация на Фурие (FTIR). Ефектите на различни температури и концентрации върху размера на нанокристалитите също бяха изследвани по метода на рентгенова прахова. Диелектрична константа (K) и капацитет (C) се измерва като се използва GPS 132 A техника. Получените резултати показват, че *(PS) /* La_2O_3 нанокомпози има аморфна структура, при най-високата концентрация и най-ниската температура, която може да намали изтичането на ток и ток на тунелиране, поради високата си EOT (еквивалентна оксидна дебелина). Той може да се използва за бъдещи OTFT гъвкави устройства.