

Morphologic and optical characterization studies of the influence of reduced graphene oxide concentration on optical properties of ZnO-P₂O₅ composite sol-gel films

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We report the sol-gel spin coated method applied for preparation of ZnO-P₂O₅-rGO films with 1.0, 1.5 and 2.0% rGO content in precursors 'suspensions. All films presented rice-like grains of ZnO with average dimensions 30-40 nm regardless the concentration of rGO. AFM and SEM morphologic studies were done. The UV/VIS/NIR transmission spectra indicate high film transparency up to 80% for film deposited on ITO and up to 90% for films deposited on clear substrate. Spectroscopic ellipsometry method allowed with success the determination of thickness and optical constants of the film deposited on ITO covered glass substrate. The use of Tauc-Lorentz dispersion oscillator for modelling the optical constants was appropriate.

(Received June 28, 2019; accepted August 20, 2019)

Keywords: Sol-gel, Thin films, Graphene, Spectroscopic Ellipsometry, Zinc oxide

1. Introduction

The coupling of graphene oxide / reduced graphene (GO/rGO) with some semiconductors, in particular, zinc oxide (ZnO) was reported to be used for the inverted structure of hybrid solar cells, transparent electrode in optoelectronic devices, photocatalytic active devices, and sensors. Zinc oxide is known to have a large exciton binding energy, a wide band gap at room temperature, piezoelectricity, catalytic activity, low cost in production, bio-compatibility, environmentally friendly and chemically stable. Therefore, it has a wide range of applications like transparent electrodes [1], gas sensors, dilute magnetic semiconductors, window layer for solar cells, active channel layer of transparent thin film transistor, photocatalysts [2] surface acoustic wave devices, microsensors and photodetectors, to mention just a few of the reported applications [3-6].

In our previous studies [7] we proposed a low-cost, facile, and scalable technique to produce composite materials based on ZnO and rGO. The presence of P₂O₅ in the rGO doped ZnO films prepared by sol-gel were reported to induce a higher refractive index and extinction coefficient giving evidence with a more compact layer of rGO-ZnO-P₂O₅ as compared with rGO-ZnO. Several studies have been conducted in order to obtain the complex refractive index of graphene based ZnO-P₂O₅ composite materials, by spectroscopic ellipsometry [8-15].

In this research paper we present our studies referring to the influence of the concentration of rGO in composite layers of ZnO-P₂O₅ on optical properties and morphology of films deposited by sol-gel spin coating method.

2. Experimental

ZnO-P₂O₅-rGO nanocomposite were synthesized by spin coating sol-gel method. Zinc acetylacetonate, (Zn(C₅H₇O₂)₂·1H₂O, 99.98 wt.% Sigma Aldrich), monoethanolamine (MEA) (C₂H₇NO, Alfa Aesar) triethyl phosphate (TEP)(C₆H₁₅O₄P, 99.8 wt.%, Sigma Aldrich), distilled water, ethanol (C₂H₅OH, 96±2wt.%, Alfa Aesar) were used without previous purification. Reduced graphene oxide (rGO) in ethanol solution with concentration of 18 mg/ml solution was prepared as previous reported [16]. ITO coated glass of the type ITOGLASS12 was purchased from VisionTek Systems Ltd. and was prepared to be used as substrate for sample deposition by washing several times with ethanol and water and drying. Zinc acetylacetonate was first dissolved in ethanol at room temperature, and then MEA was added into the solution. The molar ratio of MEA to zinc acetate (MEA/ZnAc) was kept at unit. Appropriate amount of rGO suspension and TEP were added and the resulted sol was aged at room temperature for 72 hours under continuously magnetically stirring. The molar ratio ZnO/P₂O₅ was kept at 9. Sols with gravimetric concentrations of 1.0%, 1.5% and 2.0% of rGO in ZnO-P₂O₅ matrix were fabricated. The sols formed were deposited on previously cleaned thoroughly and dried ITO coated glass substrate, by spin coating at a rotation rate of 2000 rpm, at room temperature. The samples were deposited onto glass and ITO coated glass in a six-layered structure to increase the film thickness. After each spin coated layer, the samples were placed on the hot plate at 80°C for three minutes. After the six layers deposition of ZnO-P₂O₅-rGO, the samples were dried at 200°C (5°C/h)

and annealed at 400°C (500°C/h). The composition of samples in precursors 'suspension is presented in Table 1.

Table 1. The samples denomination and their gravimetric percentage in the precursor's suspension

Sample Name	ZnO , % (gravimetric)	P ₂ O ₅ , % (gravimetric)	rGO , % (gravimetric)
ZnO-P ₂ O ₅ -A rGO	87.5	11.5	1.0
ZnO-P ₂ O ₅ -B rGO	87	11.5	1.5
ZnO-P ₂ O ₅ -C rGO	86.5	11.5	2.0

Morphological investigations were made with an atomic force microscope XE-100 type form Park Systems. SEM investigations were carried out using a FEI Inspect F50 system. Optical properties were performed with a UV/VIS/NIR Spectrophotometer Perkin Elmer Lambda 1050 and ellipsometric investigations were performed with

Horiba Jobin Yvon Ellipsometer UVISEL. It is well-known that spectroscopic ellipsometry is a non-destructive and sensitive characterization method for the optical properties of materials [17-21].

3. Results and discussions

The scheme of the sol-gel process that involve the reactions of zinc acetylacetonate and triethyl phosphate hydrolysis followed by condensation with the embedment of rGO is presented in Fig. 1.

The AFM images of samples are presented in Figs. 2-4. The ZnO-P₂O₅-rGO prepared films consisting of 6 layers with 1.0, 1.5 and 2.0 % rGO concentration respectively are homogeneous with the root-mean-squared roughness (Rq) in the interval of 37-43 nm. The decrease of Rq with increasing rGO concentration could be due to the more homogeneous covering of the substrate with rGO sheets on which Zn-O and Zn-O-P-O were attached.

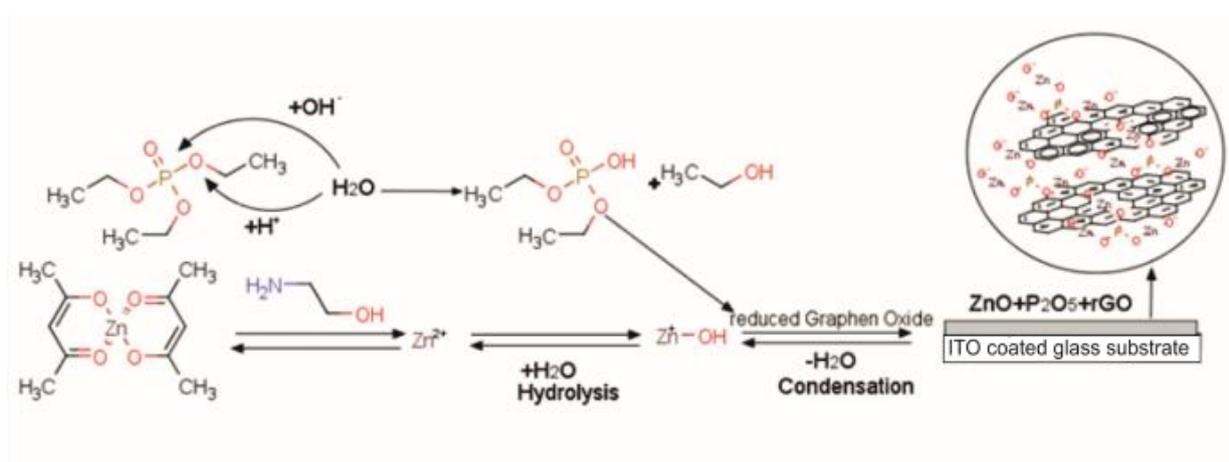


Fig. 1 Schematic presentation of hydrolysis- condensation reactions (color online)

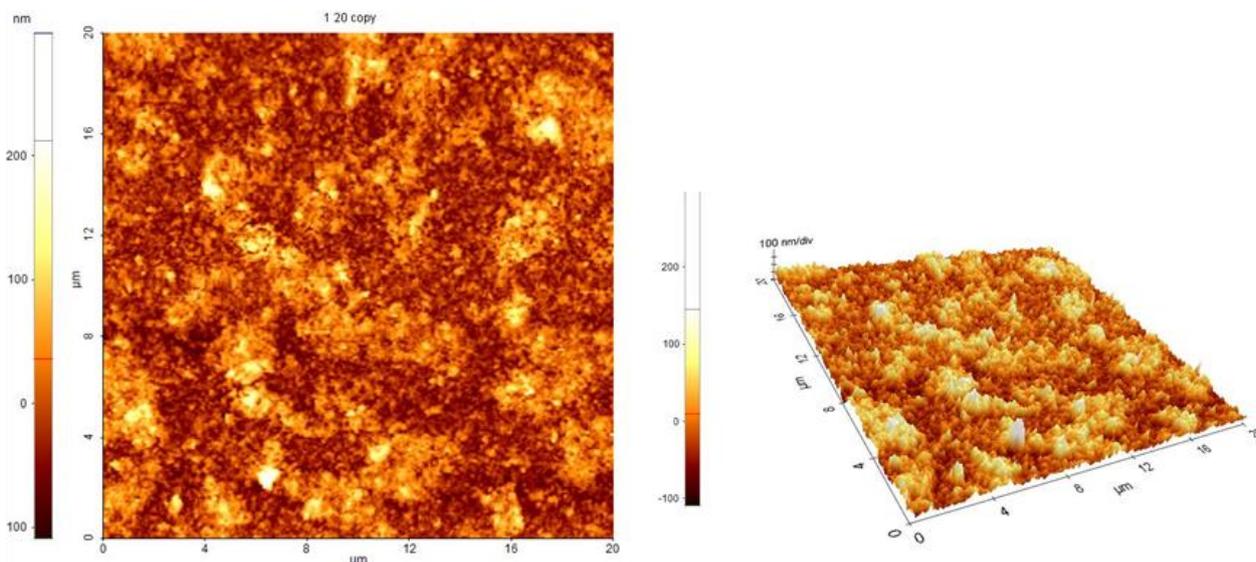


Fig. 2. AFM images of 6 layer of ZnO-P₂O₅-ArGO-films (color online)

SEM images presented in Figs. 5, 6 revealed a nanostructure of rice-like grains with average dimensions of 30-40 nm. The dimensions of grains do not vary with rGO concentration, as expected. However, the substrate was more crowded with nanostructures as the concentration of rGO increased and, therefore, looks smoother. AFM and SEM investigations suggest that rGO is more likely to attach to the surface of substrate while ZnO will prefer to grow on rGO and thus will fill the area of the sample depending on the rGO concentration. EDX investigations performed at one edge of the sample where the rGO big sheets agglomerates during the spin coating showed the presence of Zn, O and C.

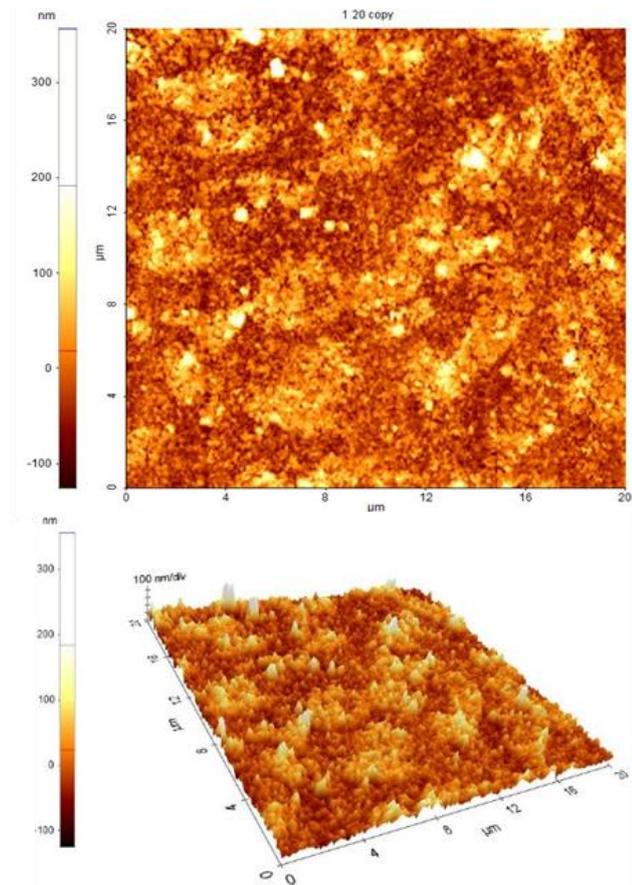


Fig. 3. AFM images of 6 layer of ZnO-P₂O₅-B rGO films (color online)

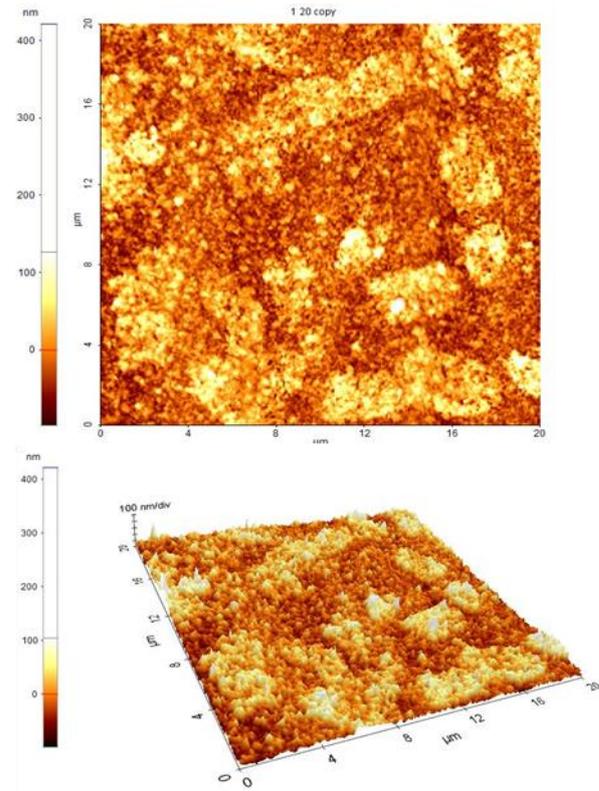


Fig. 4. AFM images of 6 layer of ZnO-P₂O₅-C rGO films (color online)

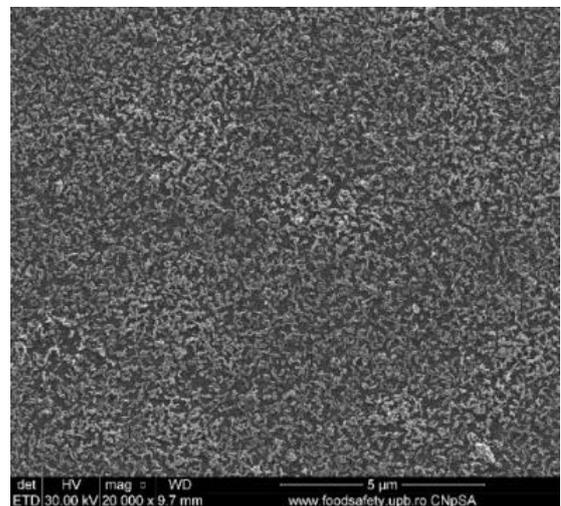


Fig. 5. SEM image of a 6-layer film of ZnO-P₂O₅-A rGO,

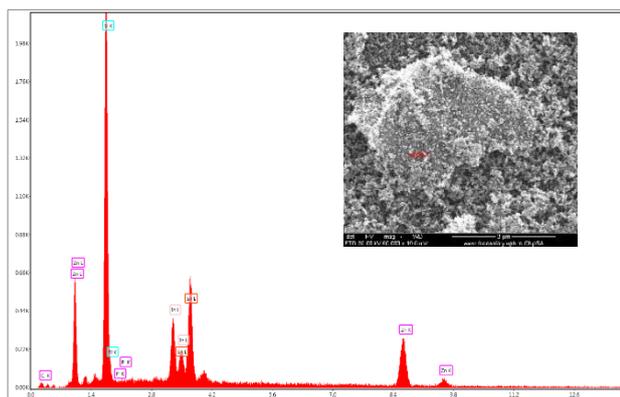


Fig. 6. SEM image and EDX spectra of a 6-layer film of $\text{ZnO-P}_2\text{O}_5\text{-C rGO}$

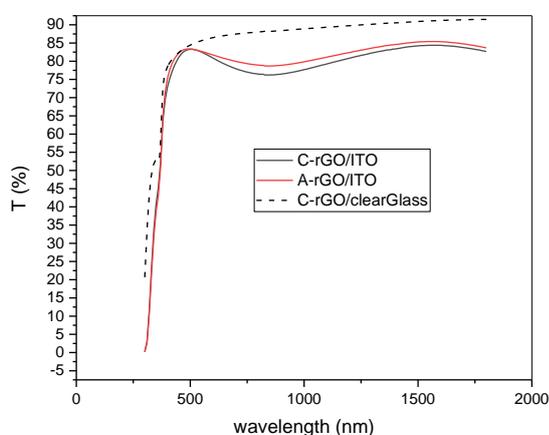


Fig. 7. Transmission spectra of 6-layer films of $\text{ZnO-P}_2\text{O}_5\text{-A, B, C rGO}$ in ITO-covered glass and on clear substrate (color online)

The UV/VIS/NIR spectra are presented in Fig. 7.

The transmissions measurements were conducted on 5 different areas of the samples and the mean values were represented on the plot. For the samples deposited on ITO coated glass, the increasing of rGO leads to the decreasing of transmission but remaining high enough around 80%. This indicates that even at 2% rGO and 6 layers, the film is suitable for transparent electrodes in solar cells. Next understanding is that the increases of rGO content in precursors 'suspension is reflected into the modification of thin film physical parameters, even if it could not be measure directly. For the samples having microscope slide substrate, the transmittance increases up to 90% and corresponds to the red curve. Small absorption peak observed at 365 nm, is belonging to the microscope slide substrate, not to the deposited thin film. As expected, all the samples showed good transparency, higher than 75% for the samples on ITO coated glass and higher than 85% for the samples deposited onto microscope slide glass [25].

Spectroscopic ellipsometry and reflectivity measurements were conducted at 70° angle, for determination of graphene oxide $\text{ZnO-P}_2\text{O}_5\text{-rGO}$ composite films of type A, B, & C corresponding to 1.0, 1.5, & 2.0 % of rGO content in precursors. The measurements were done using an ellipsometer (UVISEL, Horiba Jobin Yvon, France) [22] within the range of 190-2100 nm.

To determine the optical properties of the below studied thin films, a layer-by-layer growth model was used as presented in Fig. 9.

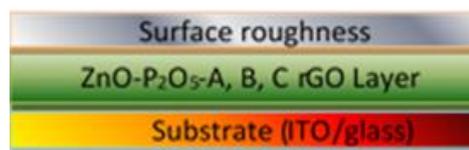


Fig. 8. Schematic illustration of model used for ellipsometric studies of $\text{ZnO-P}_2\text{O}_5\text{-A, B, C rGO}$ (color online)

The ITO film thickness is of 150 nm according to manufacturer specifications. The substrate was soda-lime glass. All calculations were performed using DeltaPsi vs 2.7 software. Substrate back reflections were eliminated by the use of a regular unreflecting black tape attached on the backside by using immersion oil. Experimental data were fitted for the transparence domain in order to find the thin films thickness. The data are presented in Table 2.

Table 2. Thin films thickness

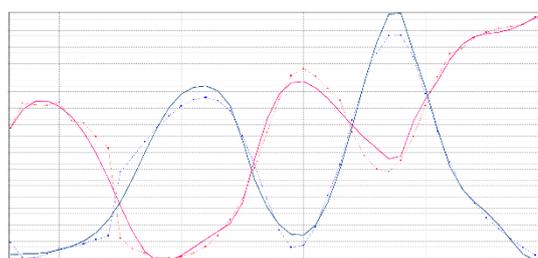
Thin film/Substrate	Thickness	Fit Range /Increment
$\text{ZnO-P}_2\text{O}_5\text{-A rGO}$	100 nm	0,6 – 6,5 eV / 0,1 eV
$\text{ZnO-P}_2\text{O}_5\text{-B rGO}$	115 nm	0,6 – 6,5 eV / 0,1 eV
$\text{ZnO-P}_2\text{O}_5\text{-C rGO}$	100nm	0,6 – 6,5 eV / 0,1 eV

The preliminary thicknesses measured on different locations by Stylus Profilometer were the following: (118,99,109) nm for A, (80,101,94) nm for B and (85,91,98) nm for C. The optical constants were modelled using a Tauc-Lorentz dispersion formula, whereas the surface roughness was modelled by mixing the optical constants of the thin film material for $\text{ZnO-P}_2\text{O}_5\text{-A, B, C rGO}$ and air. About 100 nm films thickness was used to initiate the fitting procedure.

The model $\text{ZnO-P}_2\text{O}_5\text{-A rGO}$ was: thickness: $100\text{nm} \pm 7\text{nm}$. Oscillator used was Tauc-Lorentz, number of points: 45. The MSE fit was 9.3.

The model results for $\text{ZnO-P}_2\text{O}_5\text{-B rGO}$ was: thickness: $115\text{nm} \pm 8,6\text{nm}$. Oscillator used was Tauc-Lorentz, number of points: 45. The MSE fit was 9,1.

The model results for $\text{ZnO-P}_2\text{O}_5\text{-C rGO}$ was: thickness: $100\text{nm} \pm 7,1\text{nm}$. Oscillator used was Tauc-Lorentz, number of points: 45. The MSE fit was 7.4. (see fit progress below*)



*Example of fit progress

By comparing the results regarding the refractive index presented in Fig. 9 a notable difference can be observed. The sample A with gravimetric concentrations of 1% of rGO in ZnO-P₂O₅ matrix showed higher value 2.9 of refractive index. With increasing the content of rGO the refractive index became lower, 2.6 for sample B and 2.0 for C sample. The changes are amazing high what can lead to thought that photoinduced changes can be high also. This means that films can be suitable for nonlinear optics.

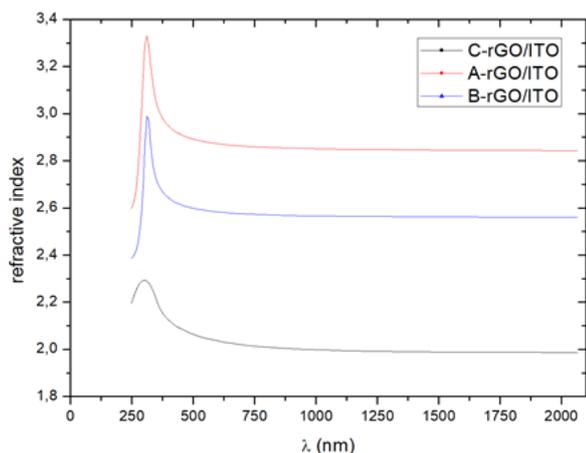


Fig. 9. Refractive index of ZnO-P₂O₅-rGO obtained by spectroscopic ellipsometry

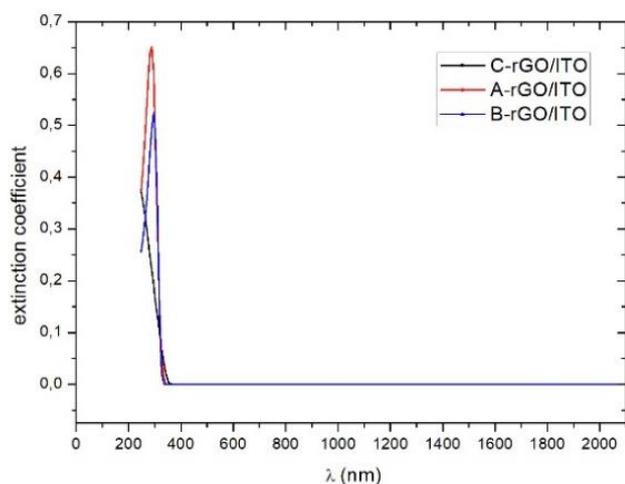


Fig. 10. Extinction coefficient of ZnO-P₂O₅-rGO composite thin films

Regarding the extinction coefficient, from the results presented in Fig. 10, it can be observed that films have low optical absorption at the wavelengths over 400 nm up to 2000 nm and are promising materials for optical devices, including transparent electrodes. The extracted dispersion curves render a refractive index and extinction coefficient for the ZnO-P₂O₅-rGO layer that corresponds well with properties previously reported for the characterized thin films [23-24].

4. Conclusions

Homogenous ZnO-P₂O₅-rGO films with 1.0, 1.5 and 2.0% rGO by sol-gel spin coated method were prepared.

All films presented rice-like grains of ZnO with average dimensions 30-40 nm.

The dimensions of grains do not vary with rGO concentration. However, the substrate was more crowded with nanostructures when the rGO concentration increases.

The optical transmission of thin films deposited on ITO covered substrate is high enough, around 80%. The transmittance increases up to 90% for films deposited on clear substrate.

The extracted dispersion curves render high of 2.9 refractive index for 1% rGO films which decreases to 2.0 for 2% rGO. The extinction coefficient shows high optical transparency of the films for wavelength higher than 400 nm

Spectroscopic ellipsometry method allowed with success the thickness and optical constants determination of developed thin films with very high accuracy even were films have nm thick and were deposited on ITO-glass substrate. The use of Tauc-Lorentz dispersion oscillator for modelling the optical constants was appropriate.

Acknowledgments

The authors are grateful to UEFISCDI (Executive Unity for Financing of Higher Education, Research and Innovation) for the financial support of projects 42PCCDI/2018, 47PCCDI/2018, Core Program, project PN 18N/08.02.2019, grant MNET17 /NMCS0042, contract 19PFE/17.10.2018 and contract number 31 and 98 MANUNET / 2018 and 2019.

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