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SPECTROSCOPIC ELLIPSOMETRY STUDIES OF PHOSPHORUS OXIDE INFLUENCE ON GRAPHENE-ZnO SOL-GEL COMPOSITE FILMS OPTICAL PROPERTIES

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Composite materials of zinc oxide (ZnO) and graphene oxide (GO) have caused emergence of potential application in the field of optoelectronics. Phosphate based glasses (P_2O_5) can improve the conductivity and increase the graphene oxide (GO) concentration and homogeneity distribution in the films. This paper presents a comparative study of two types of composite thin films: ZnO/P_2O_5/GO and ZnO/GO deposited through a sol-gel process on glass substrates. Optical analysis derived from spectroscopic ellipsometry was involved calculating the reflectance spectral curves for different thicknesses of the thin film layers constituting the ZnO/P_2O_5/GO and ZnO/GO.

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1. Introduction

Since the graphene first discovery, it's chemical, optical, mechanical and electrical properties demonstrated its high importance for wide applications [1-3]. Bae [4] proved that graphene have potential to be used as transparent conducting electrodes for flat panel display, grown by chemical vapour deposition method on copper substrate.

This seems to be a successful method in order to develop high performance devices. In this way it is required high-tech device processes with high costs and it is best to take into consideration low costs methods as chemical synthesis in order to develop graphene for transparent applications.

Zinc oxide (ZnO), being an important wide-bandgap semiconductor, has proved excellent performances in optoelectronics and photonics systems [5-6]. In comparison with individual materials, the ZnO doped graphene thin film could prove unique properties and present some special features, such as high electrical properties, optical transmittance, improved field emission and capacitive properties [7]. Also compared with other carbon materials, graphene is a promising material due to its particular characteristics [8-10].

The P_2O_5 was reported to improve the embedment of the organic moiety in the Si–O–P–O- network [11-12].

Absorbance and optical conductivity of graphene have been measured by transmittance and reflectance [13-14]. Several studies have been conducted in order to obtain the complex refractive index of graphene by spectroscopic ellipsometry [15-23].

It is well-known that spectroscopic ellipsometry is a non-destructive and sensitive characterization method for the optical properties of materials [24-29].

In this paper ZnO/rGO and ZnO/rGO/P2O5 nanocomposite were synthesized by the sol–gel method, were r-means "reduced" GO.

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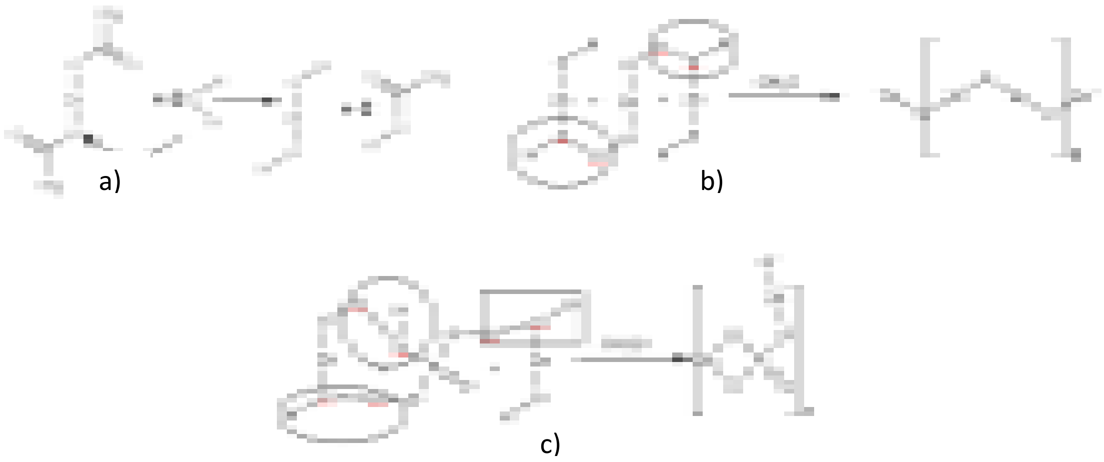
The optical analysis presented in this work involves using ray tracing methods calculations of optical spectral curves for some thicknesses of the thin film layers. These studies provide guidelines for thin films layer thickness optimization in order to trace efficient light management way for optoelectronic applications. Recent studies regarding graphene underline its high value also for industrial applications [2, 13].

2. Materials

ZnO/rGO and ZnO/rGO/P_2O_5 nanocomposite were synthesized by spin coating sol–gel method. Zinc acetate, anhydrous, (C4H6O4Zn, 99.98 wt.% Alfa Aesar), phosphoric acid (H_3PO_4, 85wt.%, Alfa Aesar), distilled water, ethanol (C_2H_5OH, 98wt.%, Alfa Aesar) were used without previous purification.

Reduced graphene oxide (rGO) in ethanol solution with concentration of 1 mg/ml solution was prepared as previous reported [30].

Mixtures of precursors TEOS/EtOH/H_2O/rGO and TEOS/EtOH/H_2O/H_3PO_4/rGO respectively were stirred in ultrasound bath for 30 minutes followed by magnetic stirring for 48 hours. Hydrolysis and condensation reactions *a*, *b* and *c* is described as follows:



Scheme 1 Hydrolysis and condensation

The sols formed were deposited on previously cleaned glass substrate, by spin coating at a rotation rate of 2000 rpm, at room temperature.

The layers were dried at 200^0C for 1 hour and then annealed for 1 hour at 400^0C.

3. Results and discussion

The thin films morphology was investigated (Fig. 1) by the use of electronic microscope Quanta Inspect F50 with electron gun, with field emission - FEG (field emission gun) having the 1.2 nm resolution and X-ray spectrometer dispersive in energy (EDS) with resolution at MnK of 133 eV.

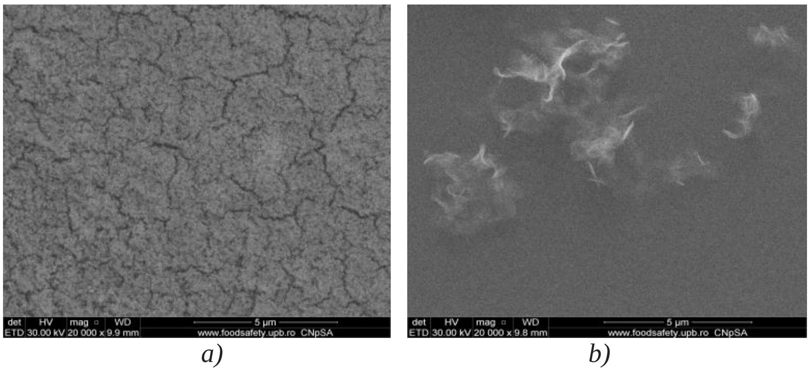


Fig. 1. (a) SEM surface view of ZnOGO and (b) $ZnOP_2O_5GO$ thin films deposited on Glass substrate with magnification of 20000x.

Spectroscopic ellipsometry and reflectivity measurements were used for determination of ZnO/GO/Glass and $ZnO/GO/P_2O_5$/Glass films thickness using an ellipsometer within the range of 190-2100 nm (UVISEL, Horiba Jobin Yvon, France) [26].

For determination of the optical properties of the below studied thin films, a layer-by-layer growth model was used as presented in Fig. 2.

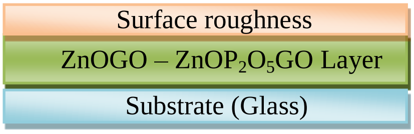


Fig. 2. Schematic illustration of 2-layer model studied for ZnOGO/Glass and $ZnOP_2O_5GO$ layer on Glass substrate

All calculations were performed using DeltaPsi vs 2.6 software. Substrate back reflections were eliminated by the use of a regular non-transparent tape. Experimental data were fitted for the transparence domain in order to find the thickness (Table 1) for both thin films:

Table 1. Thin films thickness.

No.	Thin film/Substrate	Thickness	Fit Range / Increment
1.	ZnOGO/Glass	444 nm	0,6 – 6,5 eV / 0,1 eV
2.	$ZnOP_2O_5GO$/Glass	433 nm	0,6 – 6,5 eV / 0,1 eV

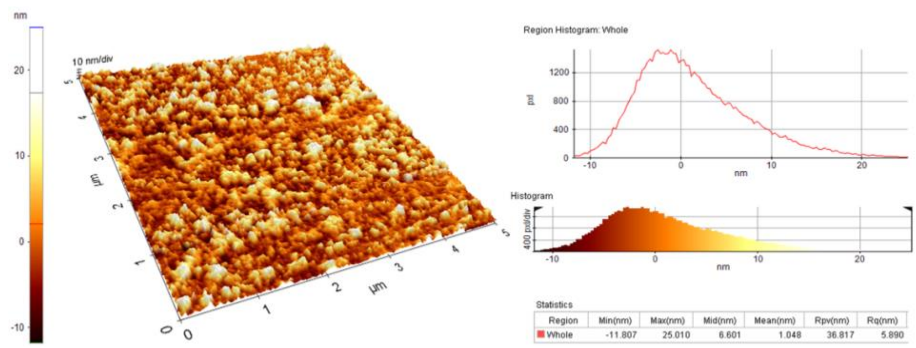


Fig. 3. AFM image of ZnO/GO thin film surface deposited on Glass substrate.

The model consists of a main material layer with a surface roughness layer. The Tauc – Lorentz dispersion law (oscillator) was used for the ZnO/GO layer, while the surface roughness layer was formed by one layer of ZnO/GO and voids. The model used is shown in Fig. 4.

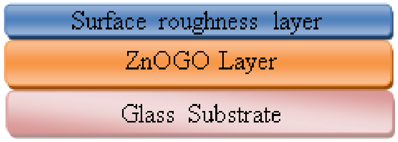


Fig. 4. Schematic illustration of 2-layer model for ZnO/GO layer on glass substrate.

The extracted refractive index *n* and extinction coefficient *k* for the ZnO/GO layer are shown in Fig. 5, corresponding well with dispersions relations for ZnO/GO/Glass thin film deposited by sol-gel on glass substrate.

The model details of ZnO/GO are: thickness: 444nm ± 13nm, oscillator used: Tauc-Lorentz, number of points: 60.

The mean squared error (MSE) for the fit was 7,2, roughness layer: 5,92nm ± 0.5 nm which is in accordance with the roughness resulted from the AFM investigation (Fig. 3) of 5,89, in this way being proved same results using two diferent characterization methods.

A Tauc-Lorentz dispersion formula was adopted for modelling.

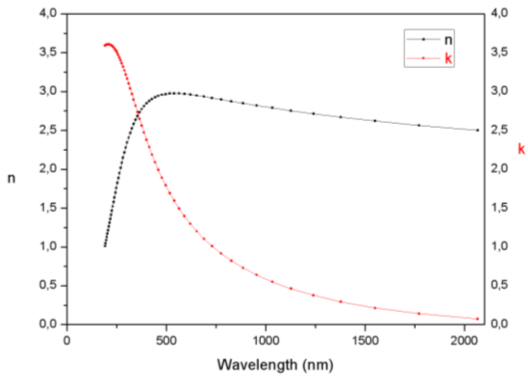


Fig.5. The refractive index and extinction coefficient of ZnO/GO thin film. The thickness of the film was 444nm ± 13 nm. The measured results were obtained from an ellipsometer within the range of 190-2100 nm (UVISEL, Horiba Jobin Yvon, France).

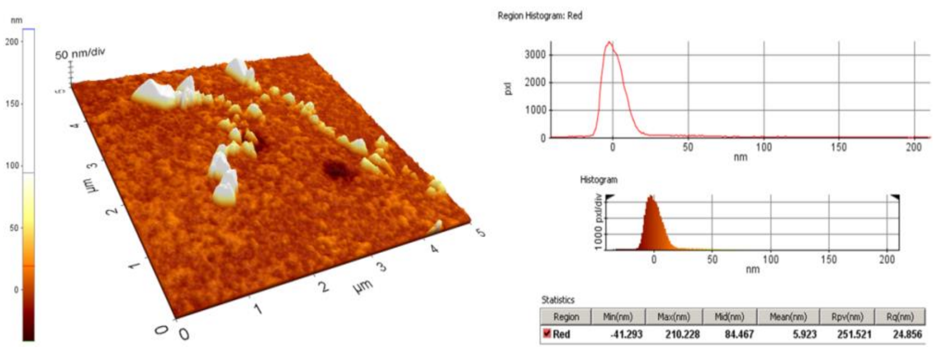


Fig. 6. AFM image of ZnO/P_2O_5/GO thin film surface deposited on glass substrate.

The model of ZnO/GOP_2/O_5 layer deposited by sol-gel on lass substrate is represented in Fig. 7.

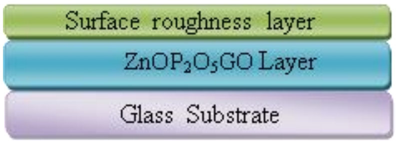


Fig. 7. Schematic illustration of 2-layer model for ZnOP_2O_5GO layer on Glass substrate.

The optical constants were modelled using also a Tauc-Lorentz dispersion formula, whereas the surface roughness was modelled by mixing the optical constants of the thin film material and air for ZnO/P_2O_5/GO/Glass, of about 430 nm thick thin film deposited by sol-gel on glass substrate are shown in Fig. 8.

The model details of ZnO/P_2O_5/GO/Glass are: thickness: 433nm ± 17nm. Oscillator used was Tauc-Lorentz, number of points: 60. The MSE fit was 1,1; roughness layer: 24,7nm ± 0.3 nm which is in accordance with the roughness of 24,8 nm resulted from the AFM investigation presented in Fig. 6, in this way being proved same results using two different characterization methods.

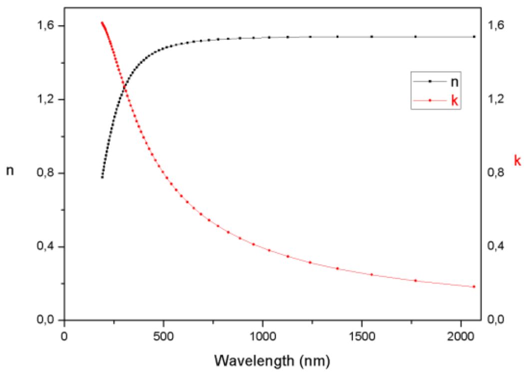


Fig. 8. The refractive index and extinction coefficient of ZnOP_2O_5GO thin film. The thickness of the film was 433nm ± 17 nm. The measured results were obtained from an ellipsometer within the range of 190-2100 nm (UVISEL, Horiba Jobin Yvon, France).

By comparing the results presented in Figs. 5 and 8 a notable difference can be observed (to see Fig. 9). This one denotes the veracity of the spectroscopic ellipsometry method concerning the characterization of optical properties for the studied materials.

The difference between the presence/absence of phosphor oxide in the ZnO/GO thin film can be explained by the following: ZnO/GO/Glass thin film obtained by sol-gel method have higher (double) refractive index and extinction coefficient than the ZnO/P_2O_5/GO/Glass thin film obtained using same method and both thin films having the same thickness.

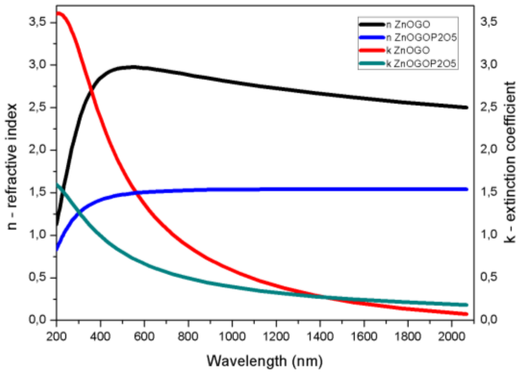


Fig. 9. The refractive index and extinction coefficient of ZnOGO and ZnOP$_2$O$_5$GO thin film on Glass substrate. The thickness of the film was 433nm ± 17 nm. The measured results were obtained from an ellipsometer within the range of 190-2100 nm (UVISEL, Horiba Jobin Yvon, France).

The extracted dispersion curves render a refractive index and extinction coefficient for the ZnO/GO layer that corresponds well with properties previously reported for ZnO/GO films [12].

4. Conclusions

The optical analysis presented in this work focused on calculating the dispersion curves for refractive index and extinction coefficient for two similar thicknesses of two thin films layers constituting the ZnO/GO and ZnO/P_2O_5/GO both deposited through a sol-gel process on glass substrates.

Optical characterization of the two thin films showed that the presence of P_2O_5 in the ZnO/P_2O_5/GO layer induces a higher (double) refractive index and extinction coefficient by comparision of ZnO/GO layer without phosphorus oxide, the simples being obtained using the same preparation method (sol-gel) and both thin films having the same thickness (~ 430 nm).

Spectroscopic ellipsometry method (equipment UVISEL, Horiba Jobin Yvon) allowed with success the thickness and optical constants determination of developed thin films with very high accuracy even were films have *nm* thick and deposited on transparent substrate.

However, the roughness layer investigated for both ZnO/GO and ZnO/P_2O_5/GO layers lead to same results using two different characterization methods as spectroscopic ellipsometry and atomic force microscopy which denotes the veracity of the spectroscopic ellipsometry method concerning thin films optical properties characterization.

The use of Tauc-Lorentz dispersion formula for modelling the optical constants was appropriate.

Acknowledgements

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