SOL-GEL NANOSTRUCTURED Al-DOPED ZnO COATINGS

S. Mihaiu[1], A. Toader[1], I. Atkinson[1], M. Anastasescu[1], M. Vasilescu[1], R. Plugaru[2] and M. Zaharescu[1]

[1]Institute of Physical Chemistry "Ilie Murgulescu" of the Romanian Academy, Spl. Independentei 202, 060021 Bucharest, Romania

[2] National Institute for R&D in Microtechnology-IMT Bucharest, PO-BOX 38-160, 023573 Bucharest, Romania

Abstract

Transparent and conducting thin ZnO films have been extensively studied due to potential applications in various fields e.g. flat panel displays, gas sensors, solar cell windows, surface acoustic wave devices, short wavelength light emitting devices, daylight-blind UV detectors[1]. In the literature data [2-3], various physical and chemical methods for obtaining the ZnO -based films are mentioned.

In the present work, mono - and multilayer Al doped ZnO coatings have been obtained by the sol-gel method on the silicon and glass supports; their structural and morphological characterization have been performed. The solutions were prepared from zinc acetate and aluminium nitrate in absolute ethanol in the presence of triethanolamine.

Structural and morphological evolutions of the coatings have been investigated by X-ray diffraction and Atomic force microscopy. After five layer depositions, the obtained coatings are polycrystalline with wurtzite type structure; the thickness of the coating is of 90 nm and the grain size between 20-40 nm. Fluorescence emission spectra indicate a decrease in the intensity of fluorescence emission bands with increasing number of deposition layers.

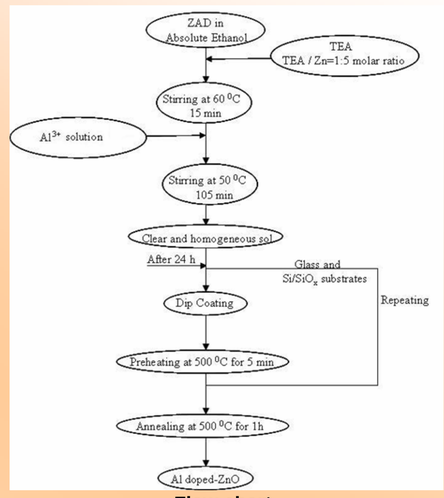
Systematic study performed allows finding most suitable chemical parameters for obtaining coatings with desired optical properties.

References

[1] Z. L. Wang *Mat. Sci. Eng.* 2009, R 64 34, 33–71
[2] T. Schuler; M. A. Aegerter *Thin Solid Films* 1999, 351, 125-131
[3] P. Sagar; M. Kumar; R.M. Mehra *Solid State Comunications* 2008, 47, 465-469

Experimental

Starting materials:
Precursors:
-Zinc acetate dihydrate (p.a) **$Zn(CH_3COO)_2x2H_2O$ (ZAD)**
-Aluminiumnitrat-nonahydrat- **$Al(NO_3)_3 \cdot 9H_2O$(ANN)**
-absolute ethanol - **CH_3CH_2OH**
-Triethanolamine - **$(CH_3CH_2OH)_3N$ (TEA)**
Initial Solutions:
-I-S-A_5ZO (0.05M of 95%ZAD and 5 %ANN in absolute ethanol and TEA with ZAD/TEA=5/1)
-II-S-A_5ZO (0.1M of 95%ZAD and 5%ANN in absolute ethanol and TEA with ZAD/TEA=5/1)
-II-S-$A_{0.5}$ZO (0.1M of 99.5%ZAD and 0.5%ANN in absolute ethanol and TEA with ZAD/TEA=5/1)
Obtained Coatings:
-I-A_5ZO-GF_n and I-A_5ZO-SF_n obtained from the **I-S-A_5ZO** solution on glass substrates (G) and on Şi/SiOx wafers (S)
-II-A_5ZO-SF_n and II-A_5ZO-SF_n obtained from the **II-SA_5ZO** solution on the glass substrates (G) and the silicon wafers (S)
-II-$A_{0.5}$ZO-GF_n and II-$A_{0.5}$ZO-SF_n obtained from **II-S$A_{0.5}$ZO** solution on the glass substrates (G) and the silicon wafers (S)
Where **n** = number of depositions



Flow chart

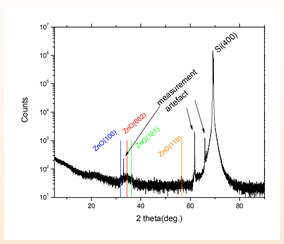
Methods of characterization

X-Ray Difracction analysis
Atomic Force Microscopy (AFM)
Scanning electron microscopy (SEM)
Fluorescence Spectroscopy
Spectroellipsometry (SE)

Results

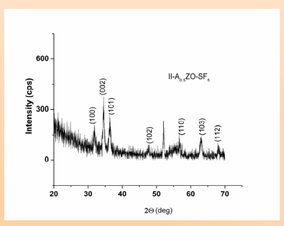
Influence of solution concentration on the coating morphology

X-Ray Diffraction



XRD pattern of the II-A_5ZO-SF_5 coating

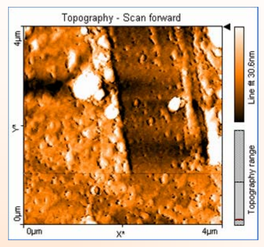
The weak intensity of the ZnO diffraction lines of indicates a low crystallization degree for the II-A_5ZO-SF_5 coating.



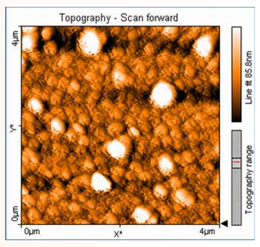
XRD pattern of the II-$A_{0.5}$ZO-SF_5 coating

The formation of ZnO polycrystalline coating indicates the XRD spectrum of the II-$A_{0.5}$ZO-SF_5 sample.

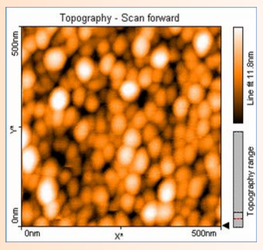
Atomic Force Microscopy (AFM)



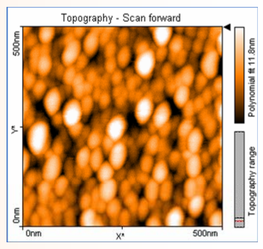
II-A_5ZO-SF_5: RMS=8.91



II-A_5ZO-GF_5RMS=18.2nm



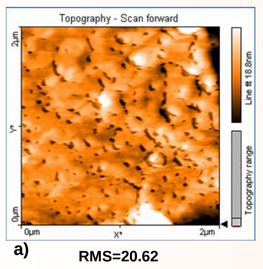
II-$A_{0.5}$ZO-SF_5 RMS=2.10nm



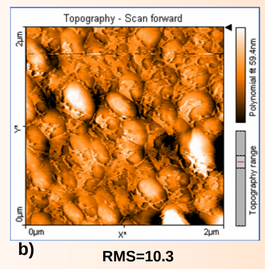
II-$A_{0.5}$ZO-GF_5 RMS=2.17nm

Influence of the substrate on the coating morphology and optical properties

Atomic Force Microscopy (AFM)



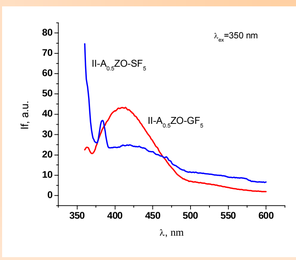
a) RMS=20.62



b) RMS=10.3

2D AFM images of the coating obtaining from II-S-A5ZO solution after five depositions:
a) II-A_5ZO-SF_5 –coating on silicon substrate
b) II-A_5ZO-GF5-coating on glass substrate

Fluorescence Spectroscopy



Fluorescence emission spectra of the coatings obtaining from the same initial solution and with the same number of depositions:
-on the glass substrate-II-$A_{0.5}$ZO-GF_5
-on the silicon wafer- II-$A_{0.5}$ZO-SF_5

Spectroellipsometry (SE)

Thickness and optical constant of the II-A_5ZO-GF_5 and II-A_5ZO-SF_5 coatings

II-A_5ZO like coating		Silicon	Glass
Thickness (nm)		29	68.7
Optical constants	n	1.38	1.80
	k	0.10	0.25

Influence of deposition number on the morphology and optical properties

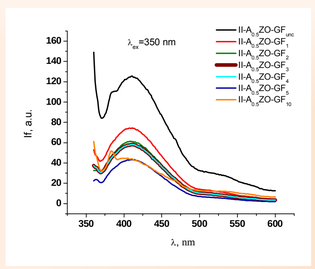
Spectroellipsometry (SE) results

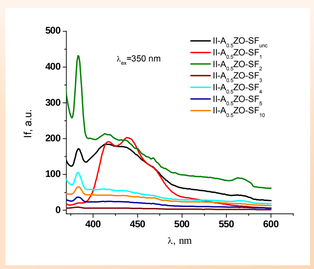
Thickness and refractive index calculated from SE data

Sample	Thickness (nm)	Refractive index-n
*I-A_5ZO-SF_{unc}	11.54	1.16
I-A_5ZO-SF_1	14.70	1.43
I-A_5ZO-SF_2	63	1.47
I-A_5ZO-SF_3	94.5	1.51
I-A_5ZO-SF_4	50.5	1.51

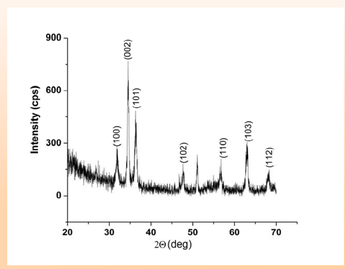
*I-A_5ZO-F_{unc}- as-prepared coating

Fluorescence spectra of the II-$A_{0.5}$ZO-GF_{1-10} and II$A_{0.5}$ZO-SF_{1-10} coatings





X-ray Diffraction of II-$A_{0.5}$ZO-SF_{10}



Conclusions

- ✓**Mono- and multilayer Al-doped ZnO coatings on the glass and silicon substrates have been obtained by dip coating sol-gel method .**
- ✓**For the same deposition number , chemical composition and concentration of the precursor solutions affects the crystallization degree of the Al-doped ZnO coatings.**
- ✓**Thinner and porous coatings with lower refractive indices are obtained on the SiOx/Si wafers compared to those deposited on the glass substrate.**
- ✓**After five layers deposition on the SiOx/Si wafers, the Al-doped ZnO coatings are crystalline with a wurtzite structure.**
- ✓**Fluorescence emission spectra of the studied samples are influenced by the precursor solutions, used substrates and number of depositions.**

ACKNOWLEDGEMENTS

The financial support of Romanian National Management Program, PN II type Project under the contract no. D11 048/18.09-2007 is gratefully acknowledged.