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Nanostructured Zn-Sn-O films obtained by dip coating technique

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Abstract

Oxide compounds belonging to Zn-Sn-O (ZTO) system with the rutile (SnO_2), wurtzite (Zn), perovskite ($ZnSnO_3$) and inverse spinel (Zn_2SnO_4) type structure with outstanding electrical and optical properties have become recently extremely attractive, to obtain transparent conducting oxide (TCO) films. It is well known that TCO films are playing an increasingly main role in many applications as transparent electrode of solar cell, the flat panel devices, infra-red (IR) reflectors, organic light emitting diode (OLED) and thin film transistor-liquid crystal display (TFT-LCD).

In the present work, stable sols with concentrations ratio of [Sn] / [Sn]+[Zn] = 0.5 and 0.33 were obtained starting from Sn(II) 2- ethylhexanoate and zinc acetate dehydrate in ethylic absolute alcohol (as solvent) and triethanolamine (as chelating agent).
Mono- and multi- layer films were deposited on glass and silicon substrates.
The structural and morphological characteristics of the as- prepared and consolidated films, were determined by IR-Spectroscopy, X-Ray Diffraction and Scanning Electron Microscopy.

The surface topography and roughness were estimated by Atomic Force Microscopy. The optical properties were determined by Spectroellipsometry measurements and Fluorescence Spectroscopy. The structure, morphology and optical properties of the obtained films depend on the composition, number of deposition and the thermal treatment temperature.

Experimental

Starting materials:

Precursors: | **Solvent** | **Chelating agent**

Sn (II) 2- ethylhexanoate (SIGMA) –$Sn(C_7H_{15}COO)_2$
Zinc acetate dehydrate (p.a) –$Zn(CH_3COO)_2x2H_2O$

Absolute ethanol (Merck)

Triethanolamine (BAKER ANALYZED) - $(CH_3CH_2OH)_3N$(TEA)

Experimental conditions for films deposition

Deposition and densification of the films	
Withdrawal speed (cm/min)/withdrawal temperature (°C)	5/20
Storage time of the sols before first deposition (hours)	24
Number of depositions	1-3
Thermal treatment of the films (°C)/time (h)	500-1

The films were labeled such as:

TZ - F whenZn-Sn-O films with Zn/Sn initial atomic ratio =1:1;
TZ_2-F whenZn-Sn-O films with Zn/Sn initial atomic ratio =2:1.
•TZ-F_{unc} and TZ_2-F_{unc} as prepared films;
• TZ-F_{nT} and TZ_2-F_{nT} consolidated films where n=1, 2, 3, 4 is the number of depositions.

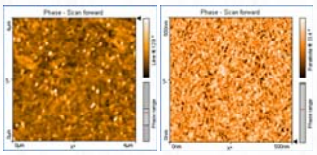
Methods of characterization

- Atomic Force Microscopy (AFM)
- Spectroellipsometriy (SE)
- The fluorescence spectroscopy

Results

Films with zinc / tin ratio 1:1

Morphology of the films



AFM image of TZ-F_{1T} films deposited on glass support

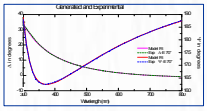
AFM image of TZ-F_{4T} films deposited on silicon wafer

Grain sizes of the TZ-F type films deposited on glass and silicon supports

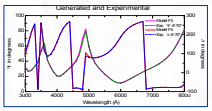
	Glass support			Silicon support		
ID	L(nm)	W(nm)	D (nm)	L(nm)	W(nm)	D (nm)
Mean	187.12	61.83	120.06	16.65	6.25	11.44
SD	152.31	36.51	80.32	5.23	1.60	2.96
Maximum	1266.1	239.75	621.69	37.31	10.93	20.76
Minimum	44.54	22.27	35.54	7.07	3. 70	5.85
Median	156.11	55.55	106.37	15.79	6.09	11.05
Mode	92.76	33.34	35.54	14.70	4.77	10.95

Optical Characteristics and thickness of the films from SE data

Cauchy Model



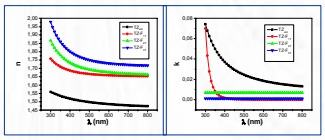
The fitted SE data for TZ-F_{1T} film deposited on glass support (generated and experimental)



The fitted SE data for TZ-F_{1T} film deposited on silicon wafer (generated and experimental)

The thickness of TZ-F type films

Films	Thickness (nm)	
	Glass	Silicon
TZ-F_{unc}	76.20	116.26
TZ-F_{1T}	38.94	28.56
TZ-F_{2T}	51.98	51.09
TZ-F_{3T}	63.15	73.62
TZ-F_{4T}	-	56.36



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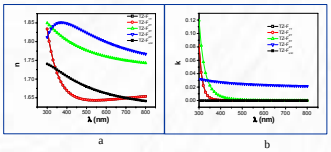
Optical constants (n,k) of the TZ-F type films deposited on glass support :
a.- refractive index (n)
b.- extinction coefficient (k)



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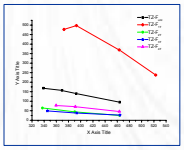
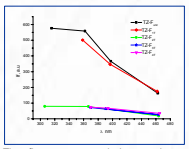
Optical constants (n,k) of the TZ-F type films deposited on silicon wafer:
a.- refractive index (n)
b.- extinction coefficient (k)

Fluorescence Properties



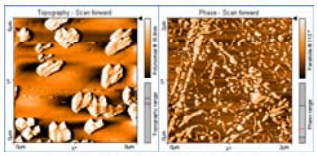
The fluorescence emission maxima, λ_{em}, and relative fluorescence intensities, I_r of the TZ-F type films deposited on glass support.



The fluorescence emission maxima, λ_{em}, and relative fluorescence intensities, I_r of the TZ-F type films deposited on silicon wafer.

Films with zinc / tin ratio 2:1

Morphology of the films



AFM image of TZ_2-F4T films deposited on glass support

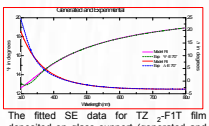
AFM image of TZ_2-F_{4T} films deposited on silicon wafer

Grain sizes of the TZ_2-F type films deposited on glass and silicon supports

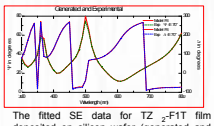
	Glass support			Silicon support		
ID	L(nm)	W (nm)	D (nm)	L(nm)	W(nm)	D (nm)
Mean	541.86	184.42	354.08	66.57	21.08	41.75
SD	476.55	156.51	303.45	66.60	15.41	34.75
Maximum	1904.40	691.75	1295.10	776.75	196.49	408.16
Minimum	89.08	44.54	71.08	11.09	5.55	8.85
Median	421.29	121.88	249.79	51.99	17.21	34.36
Mode	89.08	44.54	71.08	52.60	16.46	31.83

Optical Characteristics and thickness of the films from SE data

Cauchy Model



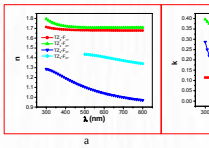
The fitted SE data for TZ_2-F1T film deposited on glass support (generated and experimental)



The fitted SE data for TZ_2-F1T film deposited on silicon wafer (generated and experimental)

The thickness of TZ_2-F type films

Films	Thickness (nm)	
	Glass	Silicon
TZ_2-F_{unc}	-	107.61
TZ_2-F_{1T}	16.65	37.44
TZ_2-F_{2T}	40.09	50.98
TZ_2-F_{3T}	36.69	89.70
TZ_2-F_{4T}	92.65	123.75



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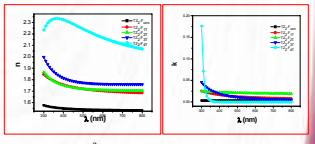
Optical constants (n,k) of the TZ $_2$-F type films deposited on glass support:
a.- refractive index (n)
b.- extinction coefficient (k)



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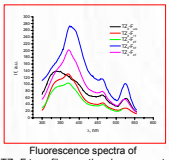
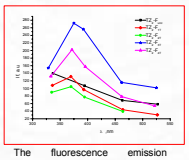
Optical constants (n,k) of the TZ $_2$-F type films deposited on silicon wafer:
a.- refractive index (n)
b.- extinction coefficient (k)

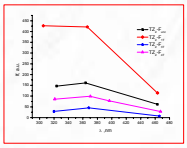
Fluorescence Properties



Fluorescence spectra of TZ_2-F type films on the glass support



The fluorescence emission maxima, λ_{em}, and relative fluorescence intensities, I_r of the TZ_2-F type films deposited on glass support.



The fluorescence emission maxima, λ_{em}, and relative fluorescence intensities, I_r of the TZ_2-F type films deposited on silicon wafer.

Conclusions

✓Adherent, continuous and homogenous films deposited on the glass and silicon supports were obtained under soft conditions by dip coating method starting from organic tin and zinc salts with zinc / tin ratio of 1:1 and 2:1.

✓The microstructure and optical characteristics of the obtained materials are strongly influenced by the Zn/Sn atomic ratios as well as the type of support used for deposition.

✓All the studied films present fluorescence emission at room temperature which depends on the number of depositions, Zn /Sn ratio and the type of substrate.

Acknowledgments

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