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CHARACTERIZATION OF ZnO AND SnO_2:F MATERIALS BY SEM FOR THEIR USE IN THE MANUFACTURE OF DSSC

Andrei CHILIAN,[a,b] Oana-Roxana BANCUTA,[a,b,*] Iulian BANCUTA,[c]
Rodica-Mariana ION,[d,e] Radu SETNESCU,[f,g] Tanta SETNESCU,[f,g] Anca GHEBOIANU,[c]
Virgil MARINESCU,[g] Cristiana RADULESCU[f]

[a] Valahia University of Târgovişte, Doctoral School, 13 Stancu Ion Str., Târgovişte, 130105, Roumania, e-mail: chilian.andrei@mail.ru
[b]The Water Company from Târgovişte, 50 I.C. Brătianu Bd., 50, Târgovişte, 130055, Roumania
[c]Valahia University of Târgovişte, Multidisciplinary Research Institute for Sciences and Technologies, 13 Sinaia Alley, Târgovişte, 130082, Roumania
[d]National Research & Development Institute for Chemistry, 202 Spl. Independentei, Bucharest, 060021, Roumania
[e] Valahia University of Târgovişte, Faculty of Materials Engineering and Mechanics, 18-24 Bd. Unirii, Târgovişte, 130082, Roumania
[f]Valahia University of Târgovişte, Faculty of Sciences and Arts, 18-24 Bd. Unirii, Târgovişte, 130082, Roumania
[g]R&D Institute for Electrical Engineering, Department for Advanced Materials, 313 Spl. Unirii, 030138 Bucharest, Roumania

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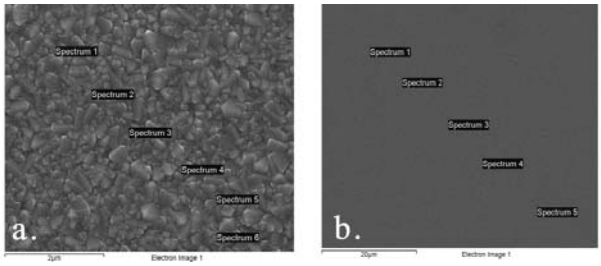
The electrodes are very important components of dye sensitized solar cells (DSSC). These components must have a high electrical conductivity and a high optical transmittance on a wide spectrum. ZnO and SnO_2:F are materials that fall into this category. By SEM it has been studied surface topography and elemental composition to identify the presence of mechanical or compositional defects. Defects of any kind of these materials can decrease efficiency and lifetime of DSSC. Applying statistical analysis to the obtained data it was possible to identify the defects of materials.



INTRODUCTION

Dye-sensitized solar cells (DSSC) continue to be a very studied area by researchers worldwide for over 20 years.[1] Their importance is accentuated by the method of preparation and the lower costs of production.[2]

In this article, it has been studied two transparent conductive materials that would be used in the preparation of dye sensitized photovoltaic cells: SnO_2:F [3] and ZnO.[4]

Transparent conducting oxides (TCO) materials are characterized by a lot of properties that require a very detailed study: resistivity, X-ray reflectivity, Hall mobility, carrier density, surface topography, optical characteristics, crystal structure and microstructure, electrical performance, chemical composition.[5]

One of the most important techniques related to the study of TCO surfaces is scanning electron microscopy (SEM).[6] This method allows the investigation of morphology and elemental composition of the material.

In the case of DSSC, it is very important that the materials used as electrodes to have a chemically uniform structure and without defects.[7]

In this study, mathematical models have been developed for identifying structural defects and to

* Corresponding author: bancuta.oana@yahoo.com

study materials using Pearson correlations, Student's t-test, principal components method (PCA), Varimax rotation method with Kaiser normalization.

EXPERIMENTAL

SEM investigations. For study TCO materials (Transparent Conducting Oxides) has been used a Scanning Electron Microscopy System with Field Emission (FESEM) coupled with Oxford Instruments INCA Energy 250 Energy Dispersive (EDS) and Focused Ion Beam (FIB) in Crossbeam Carl Zeiss Auriga device from R&D Institute for Electrical Engineering, Department for Advanced Materials, Bucharest, Roumania.

By scanning electron microscopy (SEM) was performed topographical characterization of the material and determination of elemental composition. The possibility of elemental composition determination by SEM is due to the generation of characteristic X-rays (XRF = X-ray fluorescence) by using high-current mode in SEM.

Statistical analysis. Four statistical techniques (Pearson Correlations, Student's t-test, Principal components method (PCA), Varimax rotation method with Kaiser Normalization) were used for data interpretation. Data processing was performed with IBM SPSS Statistics v.22.

Statistical techniques allow the identification of the origin of various chemical elements.

Detection of defects and possible deviations from the mean concentration was performed using Student's t-test. By this statistical method it was possible to define the concentration range of different chemical elements in TCO materials (for a 95% probability).

RESULTS

SnO_2:F material. By choosing 6 points at a distance of about 6 microns on the SnO_2: F surface with a distance between points of about 1 μm (Fig. 1), it has been determined elemental composition in these points using characteristic X rays (XRF) resulted by using high-current mode in SEM. The degree of amplification was chosen by 50 KX.

With XRF analysis has been identified four chemical elements: Sn, O, Si, Ca (Table 1).

ZnO material. For study ZnO material has been chosen 5 points at a distance about 40 μm with a distance between points of about 10 μm (Fig. 1).

With XRF analysis has been identified four chemical elements: Zn, O, Si, Ca, Sn, Mg, Al (Table 2).

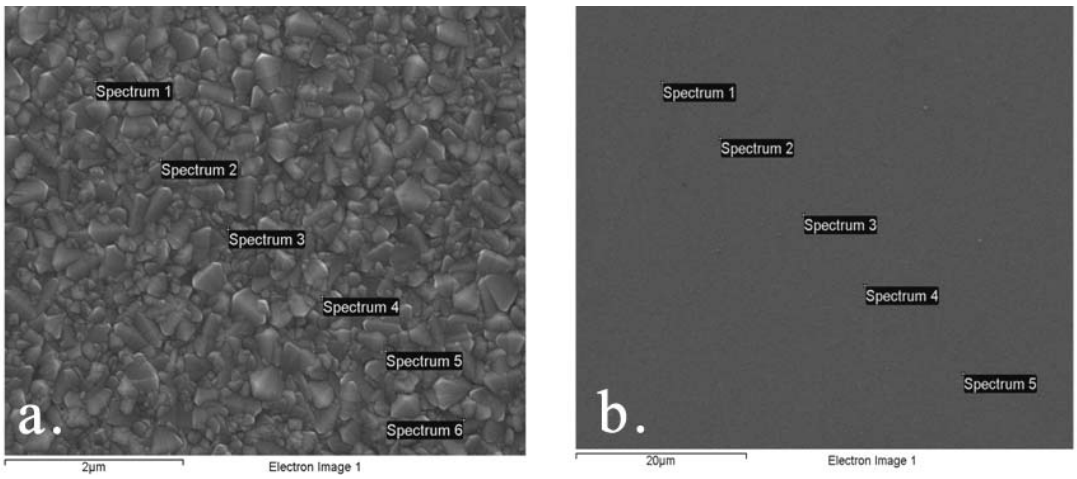


Fig. 1 – The points used for XRF determinations on SnO_2:F (a.) and ZnO (b.) materials.

Table 1

Elemental composition of SnO_2:F in 6 points

Spectrum	O (%)	Si (%)	Ca (%)	Sn (%)
Spectrum 1	***25.68***	***6.69***	1.67	***65.96***
Spectrum 2	32.44	5.23	1.64	60.69
Spectrum 3	29.41	5.98	***1.92***	62.69
Spectrum 4	***34.54***	***4.53***	1.37	***59.57***
Spectrum 5	32.55	4.72	***0.99***	61.74
Spectrum 6	27.52	5.82	1.38	65.28
Average	30.36	5.49	1.49	62.66

Table 2

Elemental composition of ZnO in 5 points

Spectrum	O (%)	Mg (%)	Al (%)	Si (%)	Ca (%)	Zn (%)	Sn (%)
Spectrum 1	33.20	0.95	0.56	***18.35***	4.60	41.34	***0.99***
Spectrum 2	33.04	1.02	0.55	18.52	4.75	40.91	1.20
Spectrum 3	32.83	1.04	0.62	18.79	4.77	***40.69***	1.26
Spectrum 4	32.53	***0.85***	***0.64***	18.95	4.61	41.23	1.20
Spectrum 5	32.45	0.97	0.53	19.03	4.73	41.19	1.10
Average	32.81	0.97	0.58	18.73	4.69	41.07	1.15

Table 3

Pearson Correlations for SnO_2:F material

	O	Si	Ca	Sn
O	1	**-0.953****	-0.408	**-0.978****
Si	-0.953**	1	0.645	**0.869***
Ca	-0.408	0.645	1	0.210
Sn	-0.978**	0.869*	0.210	1

**. $p < 0.01$, N = 6
*. $p < 0.05$, N = 6.

DISCUSSION

SnO_2:F material

By analyzing the Pearson correlations[8] (Table 3) of the chemical elements concentrations, it can be seen that oxygen concentration increase in the sample is associated with tin and silicon concentrations decrease ($p < 0.01$). Strong inverse correlation between Sn and O shows that a small change of Sn concentration will produce higher jumps of O level. This phenomenon is explained by the fact that SnO_2 has high molar mass (150.71 g/mol), but the percentage mass of oxygen in molecule is quite small (21.23%). The decrease in the concentration of tin will produce an increase of other compounds in the material. Due to smaller oxygen content in SnO_2 molecule (21.23 %) compared to its content in SiO_2 molecule (53.3%), it is clear that increase of tin concentration in the material is associated with the oxygen concentration decrease in the material. The same is true for the material of SnO_2:F ($p < 0.01$).

It can highlight a correlation between the silicon and the tin ($p < 0.05$). The correlation may result from common origin of Sn and Si. Because the studied material is a glass surface coated with SnO_2:F, it can accept that silicon is present in both layers, but in different proportions.

By Student t-test,[9] it could detect the confidence interval for each chemical element and the possible locations of the defects (Table 4). With bold-italic are highlighted deviations from the confidence interval (Table 1). Spectra 1 and 4 describe the most important deviations from the mean, so the points corresponding to these spectra have a slightly different composition from the mean concentrations.

For these points there were observed exceedances of the confidence interval in 2 points for chemical elements O, Sn, Si. The explanation of this fact can be very simple: deposition of SnO_2:F layer is made on a glass layer. Thus, the variation of Sn, Si and O levels may be caused by unevenness thickness of these two layers.

Table 4

Student's t-test for SnO_2:F material

Chemical Element	Average concentration (%)	Minimum concentration with 95 % probability (%)	Maximum concentration with 95 % probability (%)	RSD (%)
Sn	62.655000	59.99885	65.31115	±4.239326
O	30.356667	26.79893	33.91440	±11.71979
Si	5.495000	4.63332	6.35668	±15.68116
Ca	1.495000	1.15782	1.83218	±22.55385

The results regarding the elemental composition were processed by principal components analysis (PCA) and then by Varimax rotation method with Kaiser normalization[10] using three iterations (Fig. 2). Use of a rotation method after PCA can facilitate identification of the components. For the SnO_2:F material on the section of 6 microns (Fig. 1) have been identified two components. These components can refer to materials used to SnO_2:F manufacture.

Component 1 is defined mostly by Sn, and component 2 - by Ca. Although silicon is assigned more to component 1 (0.852), but it seems to be found in a lesser extent in component 2 (0.517). It may be admitted that at the basis of SnO_2: F are two materials: one based on Sn and the other based on Ca. Although the main source of Si appears to be material containing Sn, it also has been contained in the calcium-based material. Although the concentration of Si in the material is higher than that of Ca, Ca assignment to component 2 is logical that it may enter into the composition of the glass used to manufacture the material.

Sn and O are assigned to the same component, with the behavior described using Pearson correlations. Tin concentration increase (0.998) is associated with oxygen concentrations decrease (-0.967).

From PCA is observed that Si has an intermediate status between Ca and Sn, but is closer to the Sn.

Information obtained by XRF analysis of points situated at greater distance between them can provide more global information and closest to the characteristics of the analyzed material. On very small distances between analyzed points, the information may become irrelevant because there is the risk of a crystallographic defect possibility in this area.

ZnO material

A strong inverse correlation between O and Si in ZnO material has been observed on a region of 40 micrometres ($p < 0.01$) (Table 5). This can be observed from the principal component analysis (PCA). Si and O are assigned to component 2 (Table 6). Si concentration decrease, compared to O concentration increase, is due to increased concentration of other oxides.

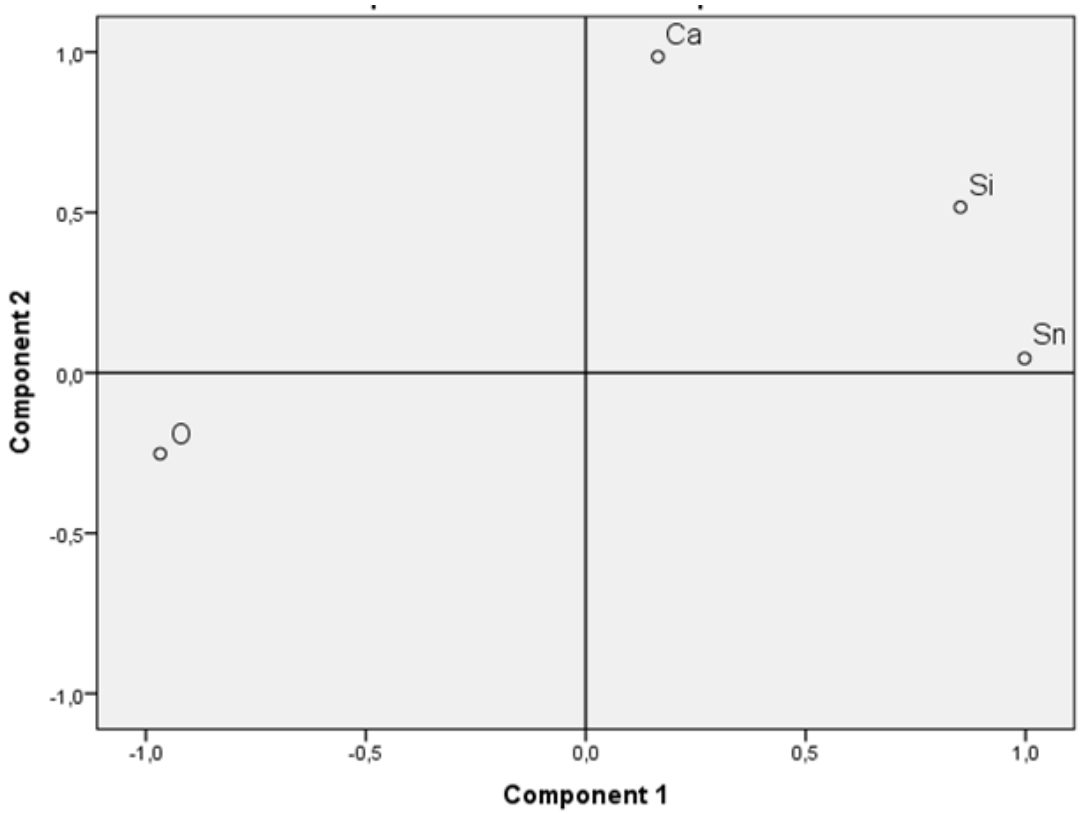


Fig. 2 – Graphical distribution of principal component analysis performed on the results of the chemical composition from Table 1.

Table 5

Pearson correlations for ZnO material

	O	Mg	Al	Si	Ca	Zn	Sn
O	1	0.405	-0.208	**-0.987****	-0.113	-0.079	-0.327
Mg	0.405	1	-0.390	-0.294	0.834	-0.748	0.234
Al	-0.208	-0.390	1	0.266	-0.235	-0.242	0.575
Si	-0.987**	-0.294	0.266	1	0.224	-0.067	0.433
Ca	-0.113	0.834	-0.235	0.224	1	-0.842	0.588
Zn	-0.079	-0.748	-0.242	-0.067	-0.842	1	-0.805
Sn	-0.327	0.234	0.575	0.433	0.588	-0.805	1

**. $p < 0.01$, N = 5.

Table 6

Principal Component Analysis with Varimax with Kaiser Normalization for ZnO

	Component		
	1	2	3
O	0.073	**-0.993**	-0.088
Mg	**0.896**	-0.322	-0.258
Al	-0.146	0.109	**0.970**
Si	0.054	**0.982**	0.157
Ca	**0.974**	0.196	-0.113
Zn	**-0.920**	0.047	-0.386
Sn	0.614	0.318	**0.687**

Table 7

Student's t-test for ZnO material

Chemical Element	Average concentration (%)	Minimum concentration with 95 % probability (%)	Maximum concentration with 95 % probability (%)	RSD (%)
Si	18.728000	18.37110	19.08490	±1.905703
O	32.810000	32.41083	33.20917	±1.216611
Mg	0.966000	0.87366	1.05834	±9.559006
Al	0.580000	0.52110	0.63890	±10.15517
Ca	4.69200	4.5917	4.7923	±2.137681
Zn	41.07200	40.7418	41.4022	±0.803954
Sn	1.15000	1.0180	1.2820	±11.47826

According to principal component analysis,[10] three components can be identified for ZnO material: component 1 (Mg, Ca, Zn), component 2 (O, Si), component 3 (Al, Sn) (Table 6). These results suggest that the ZnO matrix is given by: a Zn-based material (-0.920), Zn level increase is correlated with the decrease of Mg (0.896), and Ca (0.974) concentrations – Ca and Mg originate from the same source, it is possible from dolomite; a Si-based material (0.982) – this is the basic component of the glass; a Al-based material (0.970), with a high level of Sn (0.687).

It should be noted that the Sn is assigned in a small extent also to component 1 (0.614), which may suggest that Sn originates from two different sources.

Confidence intervals for each chemical element from the matrix show slight variations of concentration values (Table 7). The observations may indicate that the material has a relatively uniform chemical composition.

CONCLUSIONS

A TCO material with non-uniform structure can decrease the conversion ratio of light to electricity in dye-sensitized solar cells.

Using statistical methods we were able to obtain important information about the origin of the material, but also about its uniformity. Using more points on the same material, this information can be improved much more.

According to the study performed on two different TCO materials using Student t-test, ZnO has shown better chemical uniformity compared to the SnO_2:F, which may be related to different methods of obtaining these materials.

It is possible because of uneven composition of SnO_2:F, a decreased efficiency of conversion of light into electricity.

PCA provides data about the possible origin of different chemical elements from structure. This is

especially important for understanding the mechanical, optical and electrical properties of materials.

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