



THIN FILMS OF SnO₂ OBTAINED ELECTROCHEMICALLY FROM SURFACTANTS CONTAINING ELECTROLYTES

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Tin oxide (SnO₂), a n-type semiconductor is being widely used in energy production and storage devices *e.g.* dye sensitized solar cells, as transparent conductive electrode, gas sensors and photocatalytic applications – for dyes photodegradation. The paper presents a comparative study on the influence of different surfactants on the morphology of SnO₂ thin films. The samples were prepared by anodic oxidation of a tin plate in an electrolyte solution based on nitric acid. Anionic (SDS-sodium n-dodecyl sulfate) and cationic (HTAB-1-hexadecyl trimethyl ammonium bromide) surfactants were used as morphology controlling agents. The additives presence in the electrolyte solution influences the oxidation process, thus the crystal growth rate and surface morphology.

INTRODUCTION

Tin oxide (SnO₂) is a functional material, which has various technological applications including optoelectronic devices,¹ gas sensors^{1, 2} and dyes photodegradation.^{3, 4} Several methods were reported to produce SnO₂ nanoparticles and thin films, such as sol-gel,⁵ spray pyrolysis⁶ and electrochemical methods.⁷

The same material can be tailored depending on the application. A well known application is the doped thin film of SnO₂ with very uniform and dense morphology (FTO/TCO), used as substrate in the photovoltaic production. This type of morphology is needed for avoiding the shunt formation into the cell. On the other hand, for good photocatalytic efficiency, the SnO₂ thin layer should present a porous structure, thus a higher surface area for interfacial charge transfer and absorption of the incident radiation, which can lead to a photocurrent enhancement. Besides high surface area, it should possess surface hydroxide groups and other visible light active species. Moreover, the SnO₂ crystallinity improvement by annealing treatment can increase the photocurrent.

In this paper we present the results on the influence of different surfactants addition on the

morphological and chemical composition of tin oxide layers prepared by anodic oxidation. The method was chosen due to its reproducibility, and appropriate for up-scaling. The paper contains a detailed experimental study concerning the changes in morphology (surface roughness) and wetting behavior depending on the surfactant type and concentration.

EXPERIMENTAL

Precursor preparation and deposition parameters

The samples were prepared by anodic oxidation using tin plate (Merck) as a substrate. A multichannel potentiostat/galvanostat (Princeton Applied Research, model VSP) with three electrodes was used: 1 x 2 cm² tin plate as working electrode, 1 x 1 cm² platinum plate as counter electrode and Ag/AgCl/KCl_{sat} reference electrode (E = 0.197 V vs NHE).

The electrolyte solution is represented by 2 M nitric acid (99.99% HNO₃, Scharlau) and the deposition was made at 6 mA, for 3 min. Two different surfactants were added in the precursor solutions as morphology/surface properties controlling agents: (1-hexadecyl) trimethyl ammonium bromide 98%, Alfa Aesar (HTAB) and sodium n-dodecyl sulfate 99%, Alfa Aesar (SDS). The tested concentrations are presented in Table 1.

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Table 1

The additives type and concentration used for sample's deposition

| Sample | Additive | Additive's concentration |
|----------------------------|----------|--------------------------|
| SnO ₂ _0 | - | - |
| SnO ₂ _SDS_25 | SDS | 25 |
| SnO ₂ _SDS_50 | SDS | 50 |
| SnO ₂ _SDS_100 | SDS | 100 |
| SnO ₂ _SDS_200 | SDS | 200 |
| SnO ₂ _SDS_400 | SDS | 400 |
| SnO ₂ _SDS_550 | SDS | 550 |
| SnO ₂ _HTAB_25 | HTAB | 25 |
| SnO ₂ _HTAB_50 | HTAB | 50 |
| SnO ₂ _HTAB_100 | HTAB | 100 |
| SnO ₂ _HTAB_200 | HTAB | 200 |
| SnO ₂ _HTAB_400 | HTAB | 400 |

As post-deposition treatment the samples were annealed at 500°C for 3h.

Film characterization

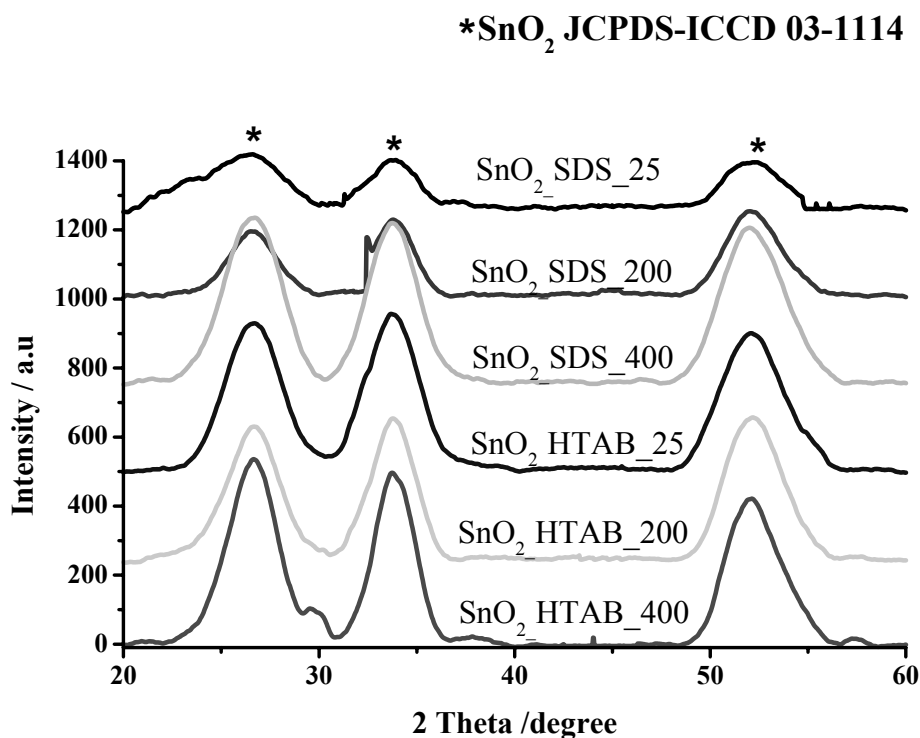
The X-ray diffraction patterns were obtained using Bruker D8 Discover Advanced Diffractometer.

The surface morphology was studied by Atomic Force Microscope (AFM, NT-MDT model BL222RNTE). The images were taken in semicontact mode with Si-tips (NSG10, force constant 0.15 N/m, tip radius 10 nm).

Static contact angle measurements, with the sessile drop method were performed using an OCA-20 Contact Anglemeter (DataPhysics Instruments). A drop (5 μ L) of glycerol (Scharlau) was placed, with 1 μ L/s velocity, on the film's surface. The surface tension of glycerol is $\sigma = 62.70$ mN/m with a polar component of $\sigma_p = 41.50$ mN/m and a dispersive component of $\sigma^d = 21.20$ mN/m, respectively.⁸

RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction spectra for representative tin oxide samples obtained with surfactant addition, after annealing. This indicates the specific diffraction lines corresponding to the formation of one single crystalline phase consisting of tetragonal tin oxide. The presence of quite wide diffraction peaks can be related with the formation of significant quantity of amorphous tin oxides (SnO, SnO₂) during the anodic oxidation process, resident in the sample even after the annealing treatments.

Fig. 1 – XRD patterns of SnO₂ layers.

The crystallite sizes were calculated using the Scherrer formula.⁹ The resulted values are almost constant for the studied samples (81.4...82.6 Å), indicating that the crystallites size is not highly dependent on the surfactant concentration for the investigated range of concentration; considering these results we may conclude that most of the crystalline phase results during annealing.

In order to tailor a material for a specific application, besides the composition, information on the surface morphology is essential. Using the atomic force microscopy, the topographies of the electrochemically deposited tin oxides layers in the absence/presence of surfactants were obtained. The AFM micrographs are given in Fig. 2 and Fig. 3.

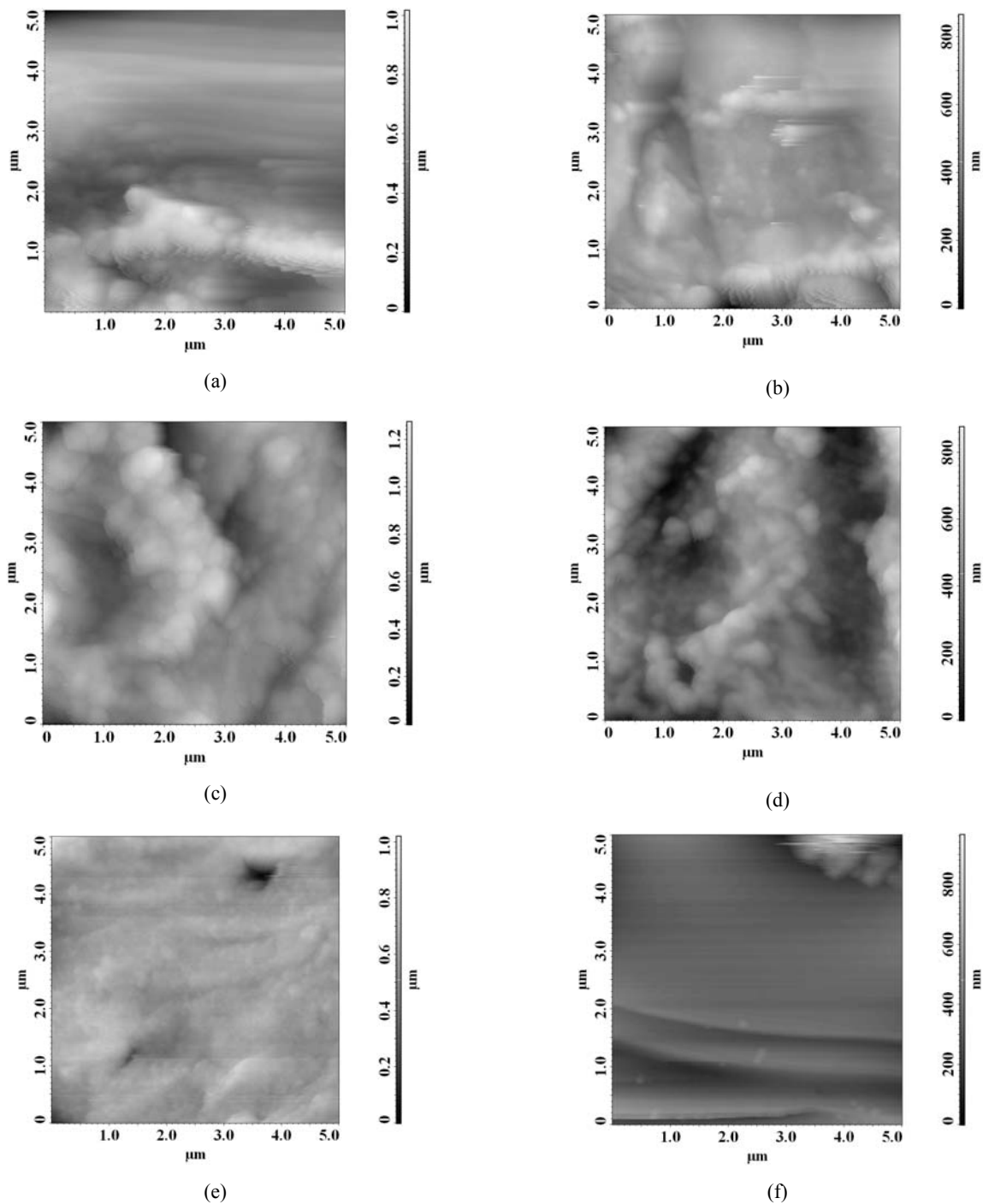


Fig. 2 – AFM images of the SnO₂ layers with SDS: (a) SnO₂_SDS_25; (b) SnO₂_SDS_50; (c) SnO₂_SDS_100; (d) SnO₂_SDS_200; (e) SnO₂_SDS_400; (f) SnO₂_SDS_550.

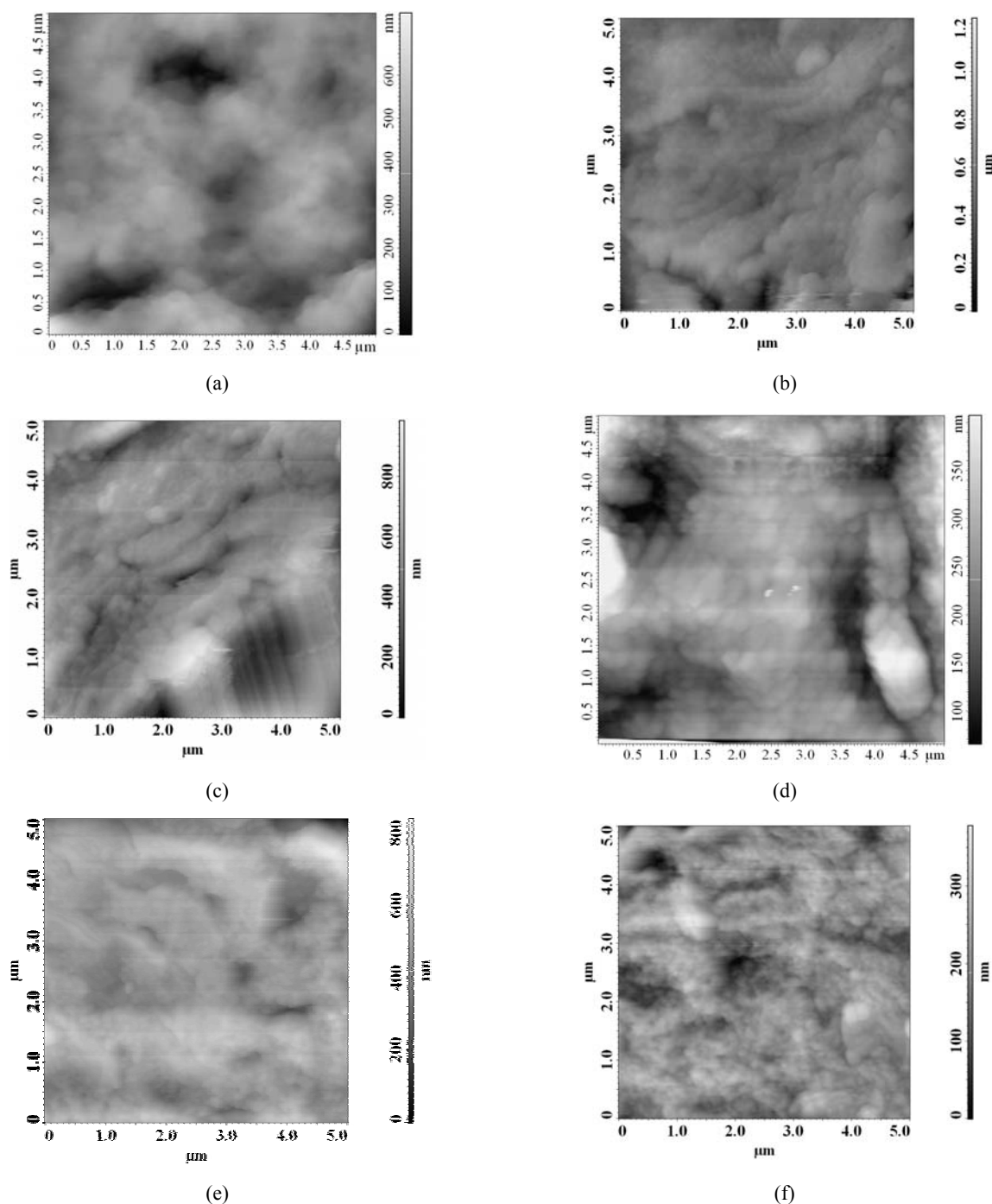


Fig. 3 – AFM images of the SnO₂ layers with HTAB: (a) SnO₂_0 (b) SnO₂_HTAB_25; (c) SnO₂_HTAB_50; (d) SnO₂_HTAB_100; (e) SnO₂_HTAB_200; (f) SnO₂_HTAB_400.

Surfactants are known to possess the ability to self assemble into aggregates (*e.g.* micelles, vesicles), which can serve for example as templates in the synthesis of a material. Thus, they can be used as morphology controlling agents for specific applications.¹⁰⁻¹⁴ In water, the investigated surfactants, with average length of the hydrophobic tail, form micelles when the critical micelle concentration (CMC) is reached. The CMC values

reported in the literature are: 1mM for HTAB at 60°C and 8.1 mM for SDS at 20°C.^{10,11} By changing the electrolyte composition or pH is possible to induce modifications in the CMC.¹¹ Moreover, due to electrostatic forces at the electrode surface micelles can form even if the surfactant concentration is lower.¹² Tailoring the SnO₂ morphology can be attempted by controlling the technological parameters of the oxidation process

(current, potential). This could explain the strong changes in morphology.

Different morphologies and surface roughness were obtained depending on the surfactant type and more important on the surfactant concentration. This dependence has almost the

same trend for the two tested surfactants and indicates a strong roughness decrease in the range of high concentrations (Fig. 4). Similar behavior is reported for other materials obtained in the presence of SDS or HTAB via electrochemical methods.^{13, 14}

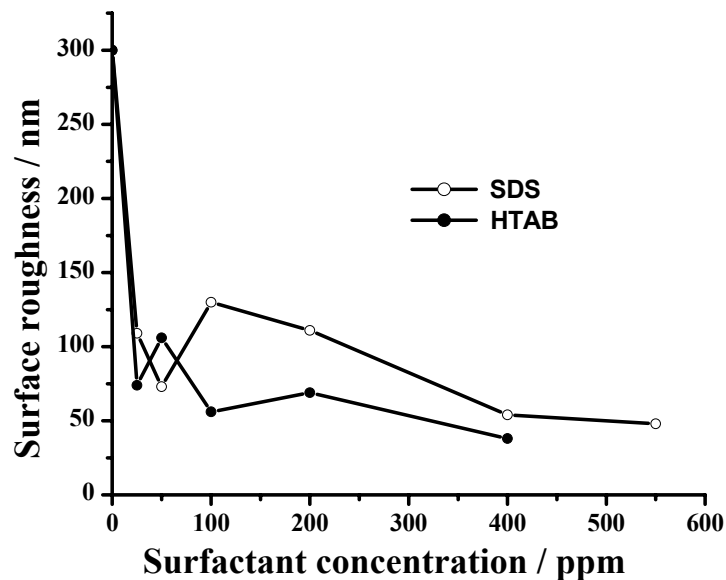


Fig. 4 – Average surface roughness of the SnO₂ thin films versus surfactant concentration.

Low concentrations of SDS lead to non-homogeneous morphologies with preferential impact on film growth, while more ordered morphologies with similar dimension of the aggregates and large macro-pores are obtained at medium SDS concentrations (100...200 ppm). High surfactant concentrations favors the nucleation rate and leads to more uniform, dense, and regulate surfaces, providing a good coverage of the tin surface.

A specific smooth morphology indicating a different growth mechanism of the tin oxide layer was observed for sample SnO₂_SDS_550 compared to the rest of SnO₂_SDS samples. This can be a consequence of the surfactant aggregates formation into the solutions as the concentration tends to CCM, influencing the electrode processes.

In the case of using HTAB, a cationic surfactant, there is no evidence of a such dramatically change in the morphology when the surfactant concentration increases, indicating that the HTAB does not exhibit a strong effect on the deposition of the tin oxide. The surface topographies are similar with those obtained when SDS is used at concentrations ranging from 100 to 400 ppm, denser as the surfactant concentration

increases. At 200 and 400 ppm HTAB, the nucleation process is predominant resulting in uniform columnar structures.

We can assume that the CCM for the investigated precursor system with SDS is between 400 and 550 ppm, while for the system with HTAB the CMC is between 200 and 400 ppm. Further investigations for the real CMC estimation in the investigated precursor solutions are necessary.

Taking into account different applications of the tin oxide, interface/ surface properties like contact angle are of importance. These properties give information on the wetting behavior and they can be correlated with the sample's topography.¹⁵⁻¹⁸ Tin oxide layer obtained with surfactant additives were characterized using the contact angle technique. The values of the contact angles measured for water are low and the adsorption rate is high, for this reason water is not recommended as a testing liquid. As consequence, glycerol with lower polarity was used. The results are presented as contact angle – time dependence in Fig. 5 and Fig. 6.

The contact angle measurements for the films obtained in the presence of SDS and HTAB indicate a strong decrease in the contact angle values comparing to the sample obtained without additives. This proves the liophile character of the surfaces,

with stronger liquid-interaction and a better wettability. The wettability depends on the interaction energy and surface roughness, respectively. Similar morphologies lead to similar contact angle behavior (*e.g.*: SDS 400 and HTAB 200).

Higher absorption/adsorption rate is observed at lower contact angle periods corresponding to a rapid filling of the large interparticle pores/voids, followed by a constant evolution of the contact angle. The adsorption/absorption occurs faster for the sample with HTAB additives, probably due to the presence of larger macro-pores. The interface behavior is controlled in the first moments mainly by the surface morphology while at longer contact time, the

interaction energy testing liquid – tin oxide surfaces are more important, but the contribution of the particle's small pores must be considered.

The trend of the contact angle – time curves are in accordance with the AFM morphologies and correspond to the European quality standards for photo-catalysts, currently under development. For the samples with HTAB additives, these lines/curves are almost parallel corresponding to similar morphologies, the difference came from the dimensions and distribution of the macro-pores, while the specific linear behavior of the SnO₂_SDS_550 sample corresponds to a very dense surface with small pores which are gradually filled.

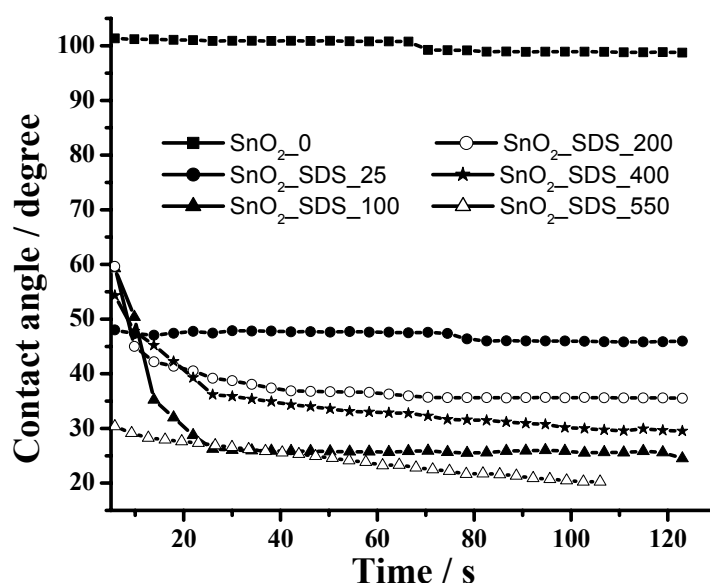


Fig. 5 – Contact angle at the interface glycerol - SnO₂ layers obtained without/with SDS additive.

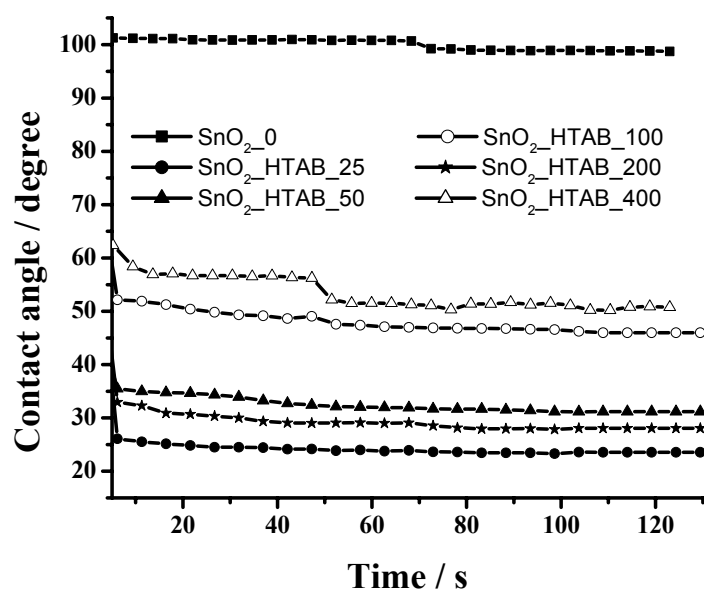


Fig. 6 – Contact angle at the interface glycerol - SnO₂ layers obtained without/with HTAB additive.

Based on the correlation structure – morphology – interface properties, recommendations for future applications of tin oxide thin layers can be done. Thus, tin oxide layers with dense, ordered structure (e.g. SnO₂_SDS_550) can be used as substrate for future deposition steps for specific PV applications, while porous structure with large pores and large interfaces (e.g. the samples obtained in the presence of HTAB, SnO₂_SDS_100, SnO₂_SDS_200) are suitable for further utilization in photocatalytic systems.

CONCLUSIONS

Tin oxide films were obtained by anodic oxidation from an acidic electrolyte solution and surfactant additives. The surfactant presence in the electrolyte solution has not a significant influence on the crystalline structures of the films, but strongly influences the surface morphology.

The contact angles measurement with glycerol indicated that the use of surfactants can be a tool of tailoring the surface wettability, according to the EU standards for photocatalysts.

Correlations structure-morphology-surface properties were developed and based on this, recommendations for further applications were given. It was proved that by using different additives in various concentrations it is possible to tailor the layer morphology and to induce changes in the surface properties (energy, wettability).

It can be concluded that the optimization of SnO₂ layer properties represents the key control for future utilization of this material in advanced electronic applications.

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