



SURFACTANT ASSISTED CONTROL OVER MORPHOLOGY AND SURFACE PROPERTIES OF SPRAYED TiO₂ THIN FILMS

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Titanium dioxide thin films are of large interest in a wide range of applications including microelectronics, optoelectronics, solar energy conversion, photocatalysis, self-cleaning coatings. The material performance is strongly influenced by the surface properties like surface energy, wettability and morphology. In this application TiO₂ thin films were deposited by spray pyrolysis on FTO substrate for solar energy applications. Crystalline thin films with regular structures and different morphologies were obtained using different surfactants, mixed in the precursor solution in a concentration of 200 ppm. The surfactants used in the study were: sodium n-dodecyl sulfate, 1-hexadecanol, 1-decanol, and (1-hexadecyl)trimethylammonium bromide. The surface morphology was studied by atomic force microscopy. Contact angle measurements have been performed to calculate the samples surface energy and to evaluate the wetting behavior of the samples. The results were correlated with the surface roughness and morphology. The films composition and crystallinity were studied using X-ray diffraction; the effect of post deposition treatment over crystallinity is also discussed.

INTRODUCTION

Nanomaterials and nanostructures have attracted much interest in the scientific world. At this scale, the properties of such materials have always been correlated with their morphology. It is a common fact that for the same material, different morphologies can induce different properties, which makes them fitted for different applications.¹ One of the most studied and used material in nanoscale applications is TiO₂.

Three polymorphs are known for TiO₂: anatase, rutile and brookite. Among these, anatase is widely researched and is used in a large number of applications thanks to its unique properties, such as optical and electronic properties, high activity, low cost, non-toxicity and chemical stability.

Titanium dioxide thin films are of interest in a range of applications including solar energy conversion systems,² photocatalysis,³ sensors,⁴ self-cleaning surfaces and a wide range of coatings. Since these applications requires specific properties for the material, TiO₂ is synthesized in films as such or from powders, using different

techniques such as: chemical vapor deposition,⁵ atomic layer deposition,⁶ electronic beam vaporization,⁷ electrostatic spray deposition,⁸ spray pyrolysis deposition,⁹ sol-gel technique¹⁰ and doctor blade technique.¹¹

The use of surfactants to control the shape and size of particles is a relatively new approach¹². The addition of surfactants in order to obtain different particles has been successfully used for the synthesis of sphere, rods, tubes, dendrites, fractals or flower like structures.¹

The aim of the paper is to present a control route of the surface properties in sprayed films of TiO₂ using additives, ionic and non-ionic surfactants, from alcoholic solutions of titanium(IV) isopropoxide.

EXPERIMENTAL

1. Deposition part

TiO₂ thin films were deposited on FTO (fluorine doped thin oxide, TEC 15/ 3mm Pilkington) conductive glass using spray pyrolysis. The glass substrates were subjected to ultrasonic cleaning through several immersions in alcohol and

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then dried with compressed air. The glass substrates were heated at the deposition temperature on a thermostatic heating plate. As precursors, alcoholic solutions of Titanium(IV)-isopropoxide TTIP (Aldrich 97%) and 2,4-Pentanedione AcAc (Alfa Aesar 99%) were used in a concentration ratio AcAc:TTIP:EtOH = 1:1.3:20 (sample A). To test the surfactants effect, samples with the same compositions were prepared by adding surfactants: the anionic Sodium n-dodecyl sulfate – SDS (Alfa Aesar 99%, Sample B), the cationic (1-Hexadecyl) trimetilammonium bromide – HTAB (Alfa Aesar 98%, Sample C) and the non-ionic 1-Decanol (Alfa Aesar 98+%, Sample D) and 1-Hexadecanol (Alfa Aesar 98%, Sample E). The surfactants concentration was 200ppm.

All samples were deposited at 400°C using compressed dried air at 1.5 bar as the carrier gas. Post-deposition treatment in open air was done for three hours at 500°C in order to improve the crystallinity of the films.¹³

2. Film characterization

The TiO₂ films deposited on FTO were analyzed using X-Ray Diffraction (XRD, Bruker-AXS-D8, Cu_{Kα1} radiation) and Atomic Force Microscopy (AFM/STM, NT-MDT model NTEGRA Probe Nanolaboratory), in semicontact mode, with a Si-tip (CSG10, force constant 0.15 N/m, tip radius 10 nm); surface energy and wetting properties were analyzed using the

Sessile drop technique for contact angle measurements with an OCA-20 Contact Angle-meter (DataPhysics Instruments). The electric behaviour of the samples was investigated by current-voltage measurements using a VSP multichannel potentiostat system Princeton Applied Research.

RESULTS AND DISCUSSION

At the selected deposition parameters the TiO₂ grow on the FTO substrate creating smooth homogenous films with no cracks or visible imperfections.

XRD patterns were recorded for sample A and for samples B, C, D, E as presented in Fig. 1. The crystallographic data show the formation of anatase TiO₂ in tetragonal system (PDF 00-021-0451) and of Ti₉O₁₇ in triclinic system (PDF 01-071-0631). The phase composition of the films and the crystallite dimensions, calculated using Scherrer's equation, are presented in Table 1.

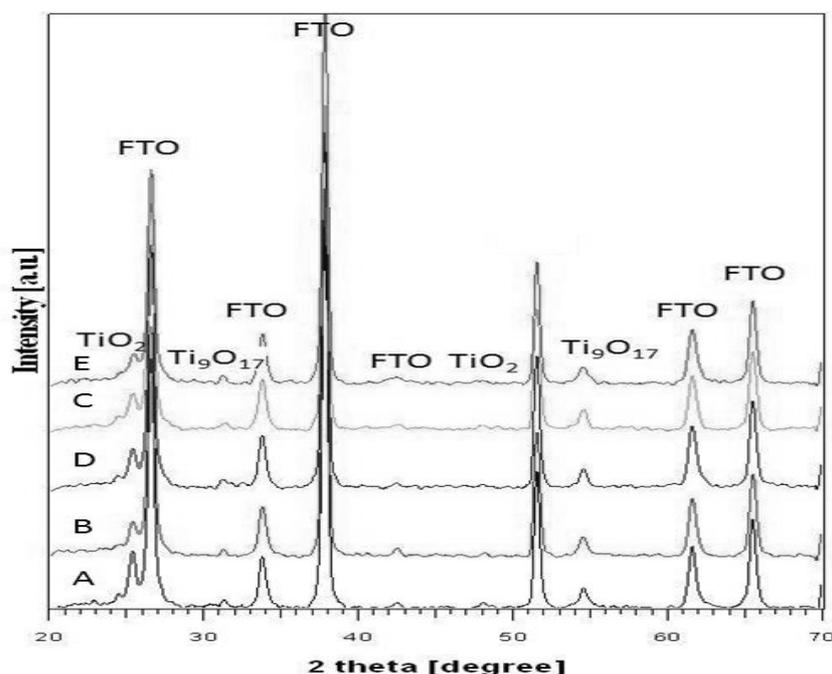


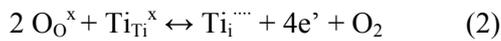
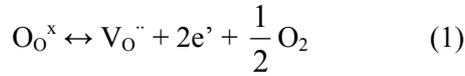
Fig. 1 – XRD patterns for sample A and samples B, C, D, E at 200 ppm surfactant concentration.

Table 1

Phase composition and crystallite dimensions for the thin films

Sample	A	B	C	D	E
Phase composition %					
TiO ₂	85.25	72.45	88.5	76.45	58.4
Ti ₉ O ₁₇	14.75	27.55	11.5	23.55	41.6
Crystallite dimension (Å)					
TiO ₂	209	304.1	102	264	172.2
Ti ₉ O ₁₇	338.9	206	338	339	100.4

The nonstoichiometric Ti₉O₁₇ phase, with lattice oxygen deficit can be explained by the following defect equations (using Kroger-Vink notations), leading to oxygen vacancies (1) or titanium interstitials (2):



These reactions are favored by high temperature and low oxygen pressure.¹⁴ Although annealing was done in air, the oxygen vacancies could not be (fully) passivated but, as the reactions show, they promote an excess of negative charge, supporting the n-type behaviour of TiO₂. We believe that this process can be avoided by a rigorous control of the O₂ pressure in the annealing chamber. The Ti₉O₁₇ phase is a suboxide, a reduced form of rutile. The nonstoichiometric forms of rutile Ti_nO_{2n-1}, Magneli phases,¹⁵ were studied as an alternative for the stoichiometric forms, having lower band gaps and fitting better to the light absorption over the visible range.¹⁶ The anatase-rutile transition is reported at temperatures above 800°C but, transition temperatures at about 500-550°C were registered for samples obtained from alcoholic precursors,¹⁷ thus we conclude that the Ti₉O₁₇ phase in the films is a consequence of the post deposition heat treatment. This effect, registered in all the samples but significant in sample E can be enhanced by the hot spots formed in/on films during heating, as a result of the combustion of surfactant traces which promote the anatase to rutile transformation.¹⁸

The AFM images recorded at 5x5 μm resolution were used in the morphology study of the films. The thin films roughness are presented in Table 2 and correspond to smooth, dense films. Sample A presents a non uniform morphology with particles of different sizes, ranging from 50 to 300nm.

The influence of the ionic surfactants in the precursor solution is observed in the morphology of samples B and C. The ionic surfactants promote a good distribution of the grain size, the aggregates have a similar shape and their size is almost identical. The shape of aggregates in the films is different for the two ionic surfactants. The film deposited from the solution with HTAB consists of round shaped aggregates, while the SDS promotes the formation of slightly more elongated grains. All the structures are well defined and the grains have an independent growth, with sizes of maximum 50nm. The use of surfactants, in amounts below the critical micelle concentration, is expected to develop self-assembled structures, insuring a more regulate volume of the droplets in the aerosol, thus more regulate nucleation and growth. Being charged, these structures repel each other, promoting distinct nucleation sites when touching the substrate. Films resulted from the solution containing the non-ionic surfactant are formed from small, rounded aggregates that adhere to one another to form more elongated structures, and the lower surface charge can be the reason for this behavior. The grains are larger and aggregate tending to form, in the case of sample E, worm like morphologies.

Table 2

Thin films roughness

Sample	A	B	C	D	E
Roughness [nm]	14.4	14.2	15.0	11.9	10.9

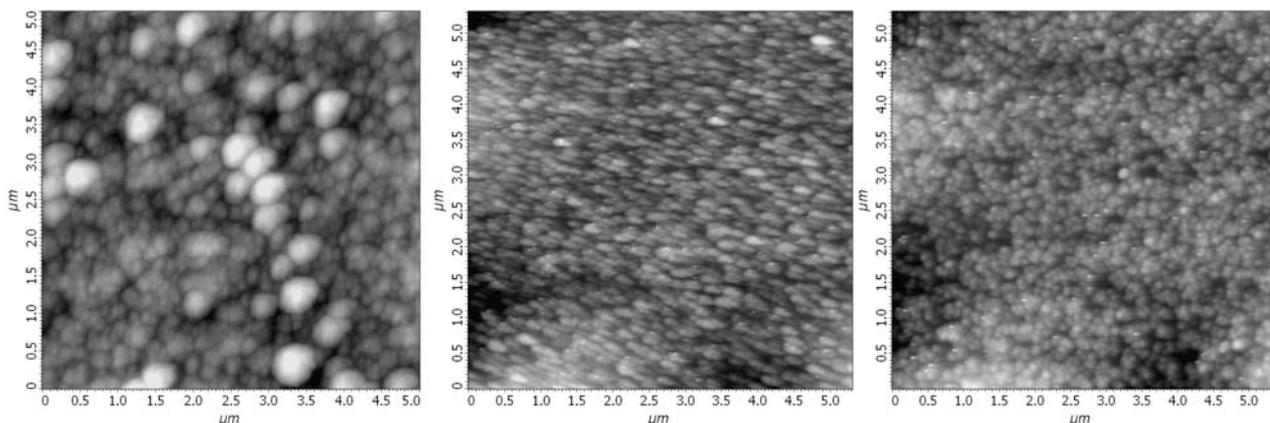


Fig. 2 – AFM images of samples A, B and C.

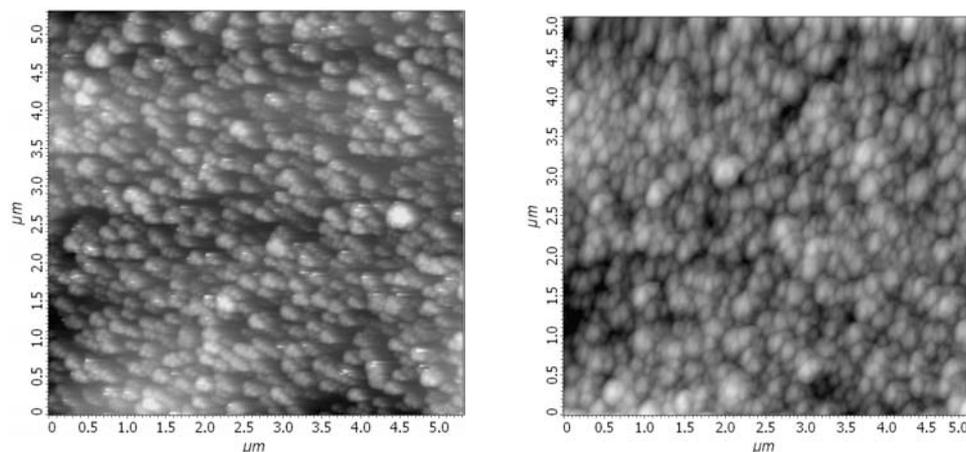


Fig. 3 – AFM images of samples D and E.

The TiO₂ semiconductor is widely used in solid state solar cells, and a good infiltration of the p-type semiconductor is a prerequisite requirement for an efficient energy conversion therefore, the surface energy and wetting capabilities of the n-type semiconductor are very important.

Contact angles were measured in 5 different points using water and glycerol as test liquids and the average values are presented in Table 3. Using the value of the initial contact angles, energy surface was calculated using the Owens-Wendt & Kaelble method.¹⁹

Using water as testing liquid shows similar values of the surface wetting behavior, corresponding to slightly polar surfaces. When ionic surfactants were added in the precursor solution, the contact angles measured with glycerol drops are larger than for the other samples, comparable to those obtained with water, proving a

good wetting capability. Their surface energy is smaller, with an increase in the polar component. This behaviour can be explained by possible ionic groups that can be formed at the surface of the sample.

The I-V curves were recorded in dark in order to test the electrical behavior of the samples. Using cyclic voltametry, a variation of the electric potential was applied to the sample from -1 to 1 V with 20 mV steps and the response in current was measured and recorded. The results are presented in Fig. 4. For the samples B, C and D the surfactants in the precursor system support the n-type behaviour. The results show that the sample containing small grains, connected in aggregates (D) have reduced losses, comparing to those with distinct grown structures (B and C). Sample E has a poor diode response, probably due to the significant amount of the Ti₉O₁₇ phase in the film.

Table 3

Surface properties of the thin films

Sample	Θ water (degree)	Θ glycerol (degree)	Surface energy (mN/m)	Dispersive component (mN/m)	Polar component (mN/m)
A	65.7	32.64	66.11	61.9	4.2
B	76.06	72.26	28.11	10.58	17.63
C	65.57	66.95	28.18	10.58	17.58
D	72.57	35.65	74.97	73.97	1
E	66.31	34.54	64.23	60.04	4.32

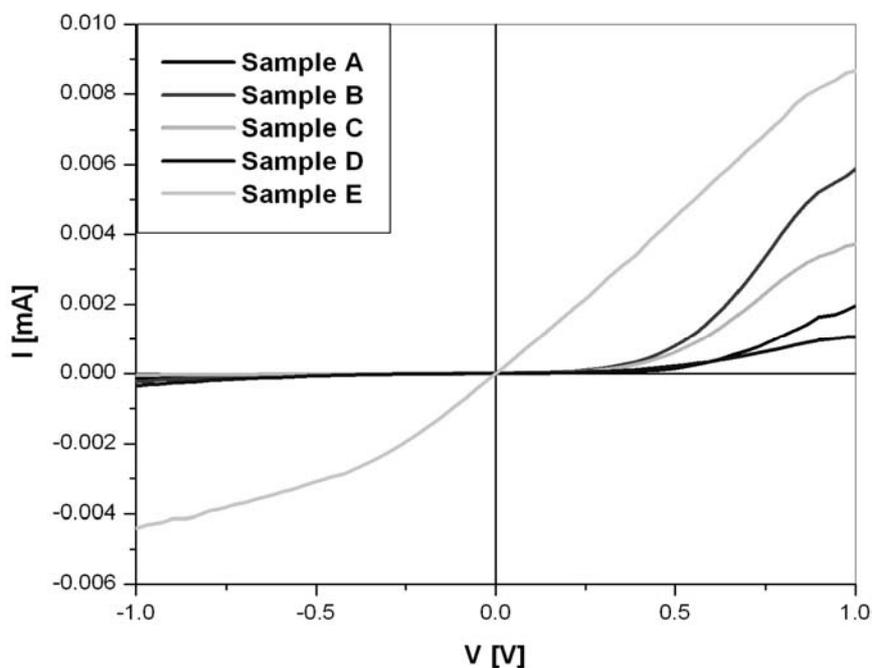


Fig. 4 – I-V curves for the thin films.

CONCLUSIONS

Thin films of TiO₂ were deposited on FTO substrates using spray pyrolysis deposition technique, from precursors containing surfactants as morphology controllers. All the samples presented a smooth, homogenous aspect with no cracks and good adhesion to the substrate.

Surfactants addition proved to promote a uniform morphology and distribution of the aggregates with similar shape and size. For samples with anionic and cationic surfactants, the formation of well defined, distinct aggregates is observed. The use of long-chained alcohols, (non-ionic surfactants) allowed the formation of merged aggregates, forming larger grains with different orientations.

The surface energy of the samples has changed with the addition of ionic surfactant, a considerable result being the increase in the polar component of the surface. The increase in the polar component encourages the infiltration of polar component on the surface of the semiconductor. Although with lower surface energy, the samples obtained using 1-Decanole presented the best electric response when testing in dark.

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