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PREPARATION AND CHARACTERIZATION OF QUASI-ONE DIMENSIONAL ATO FILMS DEPOSITED ON GLASS SUBSTRATE

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ABSTRACT. The antimony doped tin-dioxide (ATO) thin nanostructured films are known for their wide range of applications. The paper presents the preparation and characterization of quasi-one dimensional ATO films deposited on glass substrate. Films have been prepared by using the sol-gel one step multipledip-coating and spray pyrolysis techniques. Sb concentration in the precursor solution was 5 and 15 mol%, respectively. The crystalline structure of the ATO films was studied by X-ray Diffraction (XRD) which showed their polycrystalline structure with peaks belonging to the tetragonal rutil structure of SnO_2. Atomic Force Microscopy (AFM) revealed the films nanostructured morphology and different geometrical shapes of the nanoparticles depending on the route of preparation and doping degree. X-ray Photoelectron Microscopy (XPS) measurements showed that the main components at the surface of the films are: Sn, Sb, O, Cl and also that Sn and Sb are present in their oxidated state Sn^{4+} and Sb^{5+}, respectively.

Keywords: *ATO film, sol-gel technique, spray pyrolysis, crystalline structure, morphology.*

INTRODUCTION

ATO nanocrystalline thin films are well known for their use as gas sensors, transparent conductive electrode materials, catalysts, protective layers, solar cells, memory cells for fast computers [1-8]. The wide range of applications is due to the excellent mechanical, electrical and optical properties.

Literature presents several techniques for obtaining undoped and doped tin dioxide thin films on glass substrate such as: sol-gel, RF reactive magnetron sputtering, chemical vapor deposition (CVD), pulsed laser deposition

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and spray pyrolysis. Depending on the experimental conditions nanostructured films with different thicknesses, shapes (wire, ring, sphere) and dimensions of particles (20-200 nm), were obtained [9-16].

The paper reports on the investigation of structural characteristics and composition of ATO quasi-one dimensional films deposited on glass substrate prepared by using sol-gel one step multipledip-coating and spray pyrolysis techniques.

The microstructure, crystalline structure, and composition of the films were investigated by AFM, XRD and XPS.

RESULTS AND DISCUSSION

Literature shows that the thickness of ATO films obtained by sol-gel and spray pyrolysis techniques depend on number of dipping or sprayings, respectively [10, 15]. The films obtained following the routes described in the experimental section were found to have comparable thicknesses ranging in the 100.0-128.0nm domain which allows to be considered as quasi-one dimensional.

ATO films surface morphology and microstructure are affected by several experimental parameters according to the route of preparation: doping degree, annealing temperature, volume of the sprayed solution, nozzle to substrate distance, substrate temperature [11, 15].

The surface morphology and microstructure of the ATO films prepared according the described experimental conditions were investigated by AFM measurements. These revealed the films continuous character and the nanostructured morphology, as well. However, the dimensions and shapes of the nanoparticles were different depending on the route of preparation and doping degree.

The films obtained by spray pyrolysis, showed particles with spherical shape with an average diameter of 120 nm regardless the doping degree (figure 1).

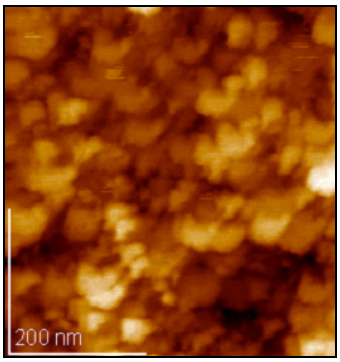


Figure 1. Typical AFM image obtained for ATO films prepared by spray pyrolysis

Films obtained by the sol-gel route, showed wire shaped (figure 2) and ring shaped particles (figure 3, a and b) depending on the doping degree. The wire shaped particles were found in films obtained by using the precursor with low content of dopand (5 mol% Sb).

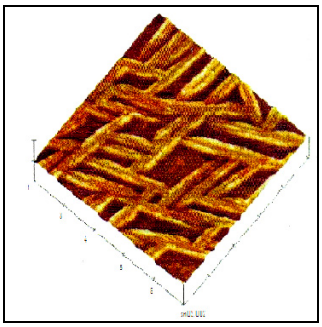
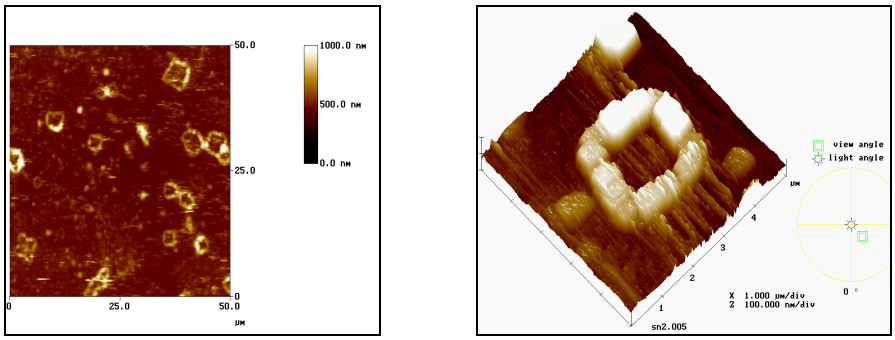


Figure 2. AFM image of films obtained by using the precursor with 5 mol% Sb:SnO_2-wire shaped particles



a **b**

Figure 3. a) 2D micrograph of films obtained by using the precursor with 15 mol%Sb:SnO_2 - ring shaped particles; b) 3D micrograph of films obtained by using the precursor with 15 mol%Sb: SnO_2 - ring shaped particle

The diameter of the ring shaped particles was found to be 850 nm, while the diameter of the wire shaped particles was 120 nm.

Literature data show that similar geometrical shapes were obtained in different experimental conditions but the dimensions of the nanoparticles were smaller [12-16]. The wide diameter of the nanorings in our samples could be assigned to a process of smaller crystallites self assembling during annealing.

The XRD patterns showed in all cases, rutile SnO_2 crystallites with tetragonal structure with a highly preferred orientation along the plane (200).

No other peaks assignable to antimony compounds were detected which means that antimony incorporation in the SnO_2 lattice has not affected the lattice structure. A typical XRD spectrum is shown in fig. 4.

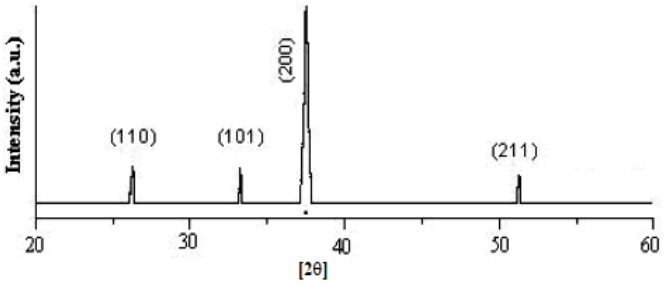


Figure 4. XRD spectrum for films obtained by using the precursor with 15 mol% Sb:SnO_2

XPS measurements have shown that the major components at the films surface are Sn, O, Sb, C and Cl. Tables 1 and 2 summarize the surface compositions of the obtained ATO films.

By flushing the film surface with a flux of Ar ions (2keV) the content of carbon decreased drastically which indicates that the presence of carbon is due to adsorption from environment. The surface presence of chlorine is due to the composition of the precursor, all salts being chlorides.

Table 1. Chemical composition of films by using the precursor with 5 mol% Sb:SnO_2

Ar flush duration (min)	(w%)				
	Sb	Sn	O	C	Cl
0	1.0	20	52	12	3.0
5	1.2	28	55	6.0	2.0
25	2.0	43	43	1.0	1.0

Table 2. Chemical composition of films obtained by using the precursor with 15 mol% Sb:SnO_2

Ar flush duration (min)	(w%)				
	Sb	Sn	O	C	Cl
0	2.5	20	50	12	2.0
5	3.0	24	48	8.0	1.5
25	3.5	40	52	1.0	1.0

The XPS investigation also revealed that on a depth of 5 nm the composition of the films is identical.

The $Sn3d_{5/2}$ and $Sn3d_{3/2}$ spin-orbital splitting photoelectrons in all samples were located at binding energies 487.5 eV and 495.3 eV (figure 5), respectively.

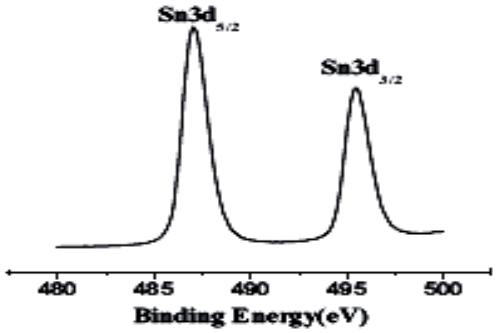


Figure 5. XPS spectrum for Sn3d peaks

The $Sb3d_{5/2}$ and $Sb3d_{3/2}$ spin-orbital splitting photoelectrons were located at the binding energies 529.5 eV and 539.5 eV, respectively. The large binding energies allow to conclude that Sn and Sb are present in their oxidate state, Sn^{4+} and Sb^{5+}, respectively.

CONCLUSIONS

Quasi-one dimensional ATO films were prepared by sol-gel one step multipledip-coating and the spray pyrolysis techniques using precursors with Sb concentration of 5 and 15 mol%. The films were characterized by using film thickness, AFM, XRD and XPS measurements. Films thicknesses ranged between 100.0-128.0nm which allows to consider them quasi-one dimensional. AFM measurements showed that the obtained films are continuous and nanostructurated, with spherical, wire or ring shaped particles depending on the route of preparation and dopand level in the precursor. The diameter of the ring shaped nanoparticles in our films was found to be higher than other reported in literature. XRD measurements revealed the tetragonal rutile crystalline structure belonging to SnO_2 with no other diffraction peaks assignable to the dopand. XPS measurements showed that the main components at the films surface are Sn, Sb, O, and Cl and that the oxidation state of Sn and Sb are Sn^{4+} and Sb^{5+}, respectively.

EXPERIMENTAL SECTION

1. Materials

$SnCl_4$ fumans (Fluka), $SnCl_4 \cdot 5H_2O$, (Sigma), $SbCl_3$ (Fluka), C_2H_5-OH, n-propanol, ammonia (Merck), reagent grade. In all cases, the substrate was a flat soda-lime-silica glass. The substrate (20x10mm) was cleaned with a neutral detergent solution, followed by rinsing with de-ionized water and acetone.

2. ATO films preparation

2.1. ***Sol-gel technique****:* the precursors were prepared as follows: $SbCl_3$ and $SnCl_4 \times 5H_2O$ mixtures with $Sb:SnO_2$ 5 and 15 mol%, respectively, were dissolved in 50 ml n-propanol under continuous stirring at 25^0C. 10 ml concentrate aqueous ammonia solution was next added drop by drop to accomplish the hydrolysis of precursor. The solution was heated to 70 C° in a water bath and stirred for four hours.

The films were obtained by one step multipledip-coating using a Nima Tensiometer. The glass slides were immersed perpendicularly into the sol with a constant speed of 5 mm/min and then withdrawn under the same conditions. The process was repeated 3 times. Immediate heating up to 500C° for one hour with a constant rate of 20^0C/min and annealing for 1 hour followed.

2.2. ***Spray pyrolysis technique****:* The glass substrate was heated in a furnace up to 500C° and kept at this temperature for 20 min. 30 ml of the precursor solution was sprayed on the substrate from 30 cm nozzle to substrate distance. The process was repeated three times at time intervals of one minute. Compressed air was used as carrier gas. The ATO layer was annealed at 360C° for 45 minutes.

3. ATO films characterization

Film thickness was measured by using Filmetrics F20.

Surface morphology and microstructure of samples were investigated by AFM in contact mode (Nanoscope type Atomic Force Microscope).

The crystalline structure was examined by XRD (Philips PW 3710 diffractometer- with CuKα source). The scanning range was $20\text{-}60^0$.

The composition of the films was investigated by using XPS (EA 125 Omicron type X-ray Photoelectron Spectrometer).

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REFERENCES

1. J. Zhu, Y. Liao, W. Jiang, *Langmuir*, **2004**, *20*, 3809.
2. S.M. Yoon, H.C. Choi, *Current Applied Physics,* **2006**, *6*, 747.
3. Z.L. Wang, *Materials Today*, **2004**, *7*, 26.
4. Y. Duan, S. Yang, H. Liu, J. Gong, H. Huang, X. Zhao, R. Zhang, Y. Du, *Journal of American Chemical Society,* **2005**, *127*, 6180.

5. X.Y. Kong, Z.L. Wang, *Nano Letters,* **2003**, *3*, 1625.
6. D. Wang, R. Xu, X. Wang, Y. Li, *Nanotechnology*, **2006**, *17*, 979.
7. J. Duan, S. Yang, H. Liu, J. Gong, H. Huang, X. Zha, R. Zhang, *Journal of Crystal Growth*, **2005**, *283*, 291.
8. J.C. Carlson, S.S. Jena, M. Flenniken, T. Chou, C.R. Wagner, *Journal of American Chemical Society,* **2006**, *126*, 7630.
9. D. Zhang, L. Tao, Z. Deng., *Materials Chemistry and Physics,* **2006**, *100*, 275.
10. D.S. Hutagalung, A.Y. Khatijah, L.B. Yeow, *Solid State Science and Technology*, **2006**, *14*, 153.
11. H. Hemissi, H. Amardjia-Adnani, J.C. Plenet, B. Canut, J.M. Pelletier, *Revue des Energies Renouvelables*, **2007**, *10*, 273.
12. D.W., Jung, D.W. Park, *Applied Surface Science*, **2009**, *255*, 5409.
13. Q. Y. Li, L.J. Wang, S.Y. Fu, *Materials Research Bulletin,* **2010**, *45*, 677.
14. J. Montero, J. Herrero, C. Guillen, *Solar Energy Mater Solar Cells,* **2010**, *94*, 612.
15. A.R. Babar, S.S. Shinde, A.V. Moholkar, C.H. Bhosale, J.H. Kim, K.Y. Rajpure, *Journal of Semiconductors*, **2011**, *32*, 102001-1.
16. W.D. Feng, W. Minghong, W. Yong, *Electrochemistry Comunications*, **2011**, *13*, 433.