THE STABILITY OF SnO$_2$:Sb (ATO) NANOSTRUCTURED PROTECTING FILMS ON GLASS

F. Kormos, I. Rotariu[a], G. Tolai[b], M. Pávai, C. Roman[c], E. Kálmán[b]

"Raluca Ripan" Chemical Research Institute, Fântânele St., no. 30, 400294, Cluj-Napoca, Romania
[a]Sanex - Lasselsberger, Beiuşului St., no 1, 400394, Cluj-Napoca, Romania,
[b]Chemical Research Center, Hungarian Academy of Sciences, Pusztaszeri St., no. 59-67, 1025, Budapest, Hungary
[c]Research Institute for Analytical Instrumentation, Fântânele St., no. 30, 400294, Cluj-Napoca, Romania

The mechanical and chemical stability of ATO (Antimony doped Tin dioxide) SnO$_2$:Sb films are recognized for their corrosion protecting capability, but their lifetime is strongly dependent on the preparation conditions. This work reports on a study of the lifetime of ATO films deposited on the glass substrate by two different techniques: CVD (chemical vapour deposition) and SG (sol-gel) method. The lifetime variation in the presence of chemically degrading medium (HCl, NaCl and tartric acid) was established by measuring the evolution of the sheet resistance, the optical transmittance in the visible region and the corrosion potential. The very low monthly corrosion rate shows a good stability for all studied degrading medium. The variation of the investigated properties proves that the films can resist for four months without significant damage.

Keywords: SnO$_2$:Sb, Coating on glass, Corrosion, lifetime

1. Introduction

Antimony doped SnO$_2$ (ATO) nanostructured films have a wide range of technological applications such as gas sensors [1], solar cells, liquid crystal display [2], luminescent lamps [3]. This material exhibits excellent properties such as resistance at high temperature, good electrical conductivity, high transparency in the visible region and high reflectivity for infrared radiation [4].

Recently, Sb:SnO$_2$ (ATO) films raised a high interest as protecting layers for architectural and automotive glass [5-8], metals [9], photosensitive membranes [10], and electrodes for lead-acid batteries [11].

The mechanical and chemical stability of ATO films is already recognized but their lifetime is strongly dependent on the preparation process. The investigation of the influence of the synthesis routes on the corrosion protecting capability of these films is, therefore, very important.

This work reports the results of a study of ATO films deposited on glass substrate by two different techniques: chemical vapour deposition (CVD) [6] and sol-gel method (SG) [12]. The lifetime of the films has been established by measuring the evolution of sheet resistance, optical transmittance and corrosion potential in the presence of some chemically degrading medium (HCl, NaCl and tartric acid).

2. Experimental

2.1. Materials

The following materials were used: SnCl$_4$ fumans (Fluka), SnCl$_4$·5H$_2$O (Sigma), SbCl$_3$ (Fluka), HCl, NaCl, C$_2$H$_5$-OH, tartric acid, n-propanol and ammonia (Merck). All these substances used were reagent grade.

2.2. Substrate

In all cases, the substrate was a flat soda-lime-silica glass. The substrate (20×10 mm) was cleaned with a neutral detergent solution, followed by rinsing with de-ionized water and acetone.

2.3. ATO films preparation

Chemical vapour deposition. The precursor solution for deposition in CVD process was an aqueous solution and was prepared using the mixture of $SnCl_4$ (3M), $SbCl_3$ (0.25M), HCl (1.5M) and ethanol (0.25M), at the end, the final solution contained 2 wt% of $SbCl_3$. The substrate was heated at 425°C and maintained at this temperature for 10 minutes, in the reactor. The carrier gas was nitrogen with a 1 l/min flow rate. The precursor solution was vaporized in the gas flow and directed to the sample surface. After 3 minutes reaction time the obtained film on the sample was cooled down in the reactor. The film was post-treated at 360°C for 45 minutes in a tubular furnace.

Sol-gel preparation. $SnCl_4 \cdot 5H_2O$ and $SbCl_3$ were dissolved in n-propanol under continuous stirring at 25°C. Dilute aqueous ammonia solution was added slowly to adjust the pH to 5-6. Then the solution was heated to 70ºC in a water bath and stirred for 4 hours. The sol was used for coating without any further operation. Coatings were obtained by one-step dip-coating process using a Nima Tensiometer. The substrate was immersed perpendicularly into the sol with a 5 mm/min constant speed and then withdrawn in the same condition. The wet layer coated substrates were heated immediately to 600°C with a constant rate of 20°C/min and annealed for 1 hour.

2.4. Characterization of coatings

Composition and crystal structure study: XRD- X ray diffraction measurements (Philips PW 3710, Kα-Cu) for CVD coatings and XPS-X ray photoelectron spectroscopy (EA 125 Omicron) for sol-gel coatings.

AFM investigation. The surface morphology of samples was investigated by contact mode atomic force microscopy (AFM). The tests were carried out using a Nanoscope Dimension 3100 AFM with a Nanoscope III a controller under software version 4.43r8[13-14].

Nanoindentation: The mechanical properties of the SnO_2 layer were measured by a Hysitron Triboscope nanointender. The intender-traducer of the equipment mounted in place of the AFM scanner in the Nanoscope Dimension 3100. Depth sensing hardness tests were performed between 4 and 12 mN load [13-14].

Electrical conductivity measurement. The sheet resistance measurement of ATO coatings was performed using the four-point method and a self-made device. The carrier charge numbers were determined by the Mott-Schottky equation, with the impedance measured at 1000 Hz. The electrochemical impedance was measured using Solartron 1286 electrochemical impedance (ECI) and Solartron 1250 (FRA). Experiments were done in a three-electrode cell using a platinum net as a counter electrode and saturated calomel electrode as a reference electrode. The working electrode was the ATO film on glass[15].

Transmittance investigation. The transmittance spectra were recorded in the 200-900 nm wavelength range using a Pye-Unicam UV-VIS spectrophotometer.

The potentiodynamic measurements were performed using a computer controlled potentiostat Model PG STAT 10 from Autolab (Netherlands) in a conventional three electrode electrochemical cell equipped with an Ag/AgCl, KCl_{sat} (Radiometer, France) as reference electrode and a platinum sheet as counter electrode. The working electrode was 1 cm^2 glass covered by ATO films. The concentration of the solutions for the chemical corrosion tests was 1M.

3. Results and discussion

The morphology and crystalline structure of ATO coatings deposited on glass is very important because the film stability is affected by the quality of the surface (uniformity, roughness,

adhesion to the substrate) and in the same time by the characteristics of the structure (crystallinity and grain size).

The surface morphology of ATO films deposited on glass substrate by CVD (Fig. 1a) and SG (Fig. 1b) was determined by AFM. The images show a dense, continuous and homogenous ATO deposits with a few superficial cracks on the surface. In addition, AFM investigations point out the uniformity of the ATO coatings on the glass. However, the thickness of ATO films prepared by sol-gel method is smaller compared to those obtained by chemical vapor deposition. The AFM images presented in Fig. 1 are maps of the surface relief in the computer memory. In the images this relief is represented in two dimensions by shading the surface as if it was lighted from the upper left corner of the image. This kind of representation emphasizes the spherical nanoparticles, uniformly distributed on the film surface. The particle size could be estimated using these images (SG-190 nm, CVD-325 nm). The sample prepared by CVD method contains larger particles in a homogeneous distribution. The SG-sample contains smaller particles also in homogeneous distribution. The larger bumps are also revealed in the figure: they are larger particles covered partly by the film. Consequently, in this film a double distribution of particles is bound in the layer.
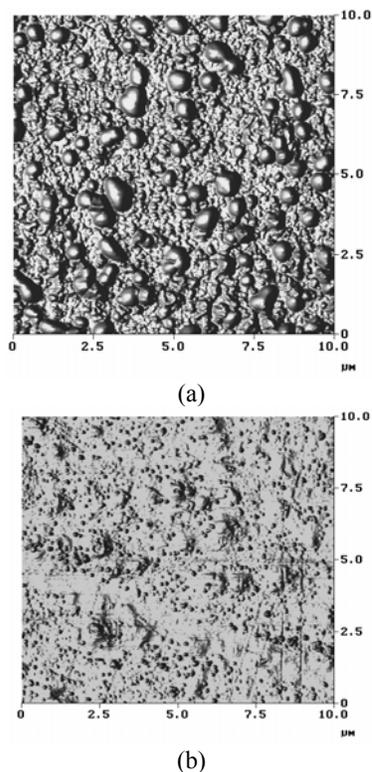

(a)

(b)

Fig. 1. AFM micrographs of CVD sample (a) and SG sample (b).

The so-called 3D images can be considered as other representation of the AFM image. Based on the maps of the surface relief in the computer memory an axonometric three-dimensional view is generated, as if the surface would be seen from close vicinity by a dedicated lighting. The Figs. 2 (a, b) show the 3D view AFM images taken on CVD (a) and on SG sample (b).
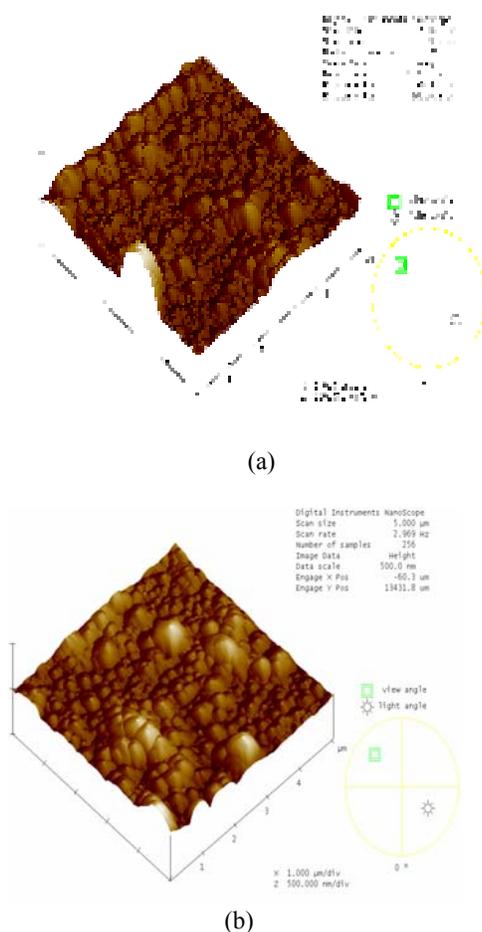
(a)

(b)

Fig. 2. 3D view AFM images of CVD sample (a) and SG sample (b).

The chemical composition of ATO films was determined using XRD technique for CVD samples and by XPS measurements for SG samples.

The XRD diagram shows the presence of the dopant antimony oxide, together with preponderant component of tin oxide (Fig. 3).

XPS measurements (Table 1 and 2) reveal that at the surface of the film the major components are based on Sn and Sb.

Table 1 show that the sample surface is contaminated by carbon and chlorine. The presence of carbon ions can be explained by the fact that they appear from the contamination of the film from the laboratory environment (organic substances, vapours). Regarding the chlorine contamination, this element originates from the precursor solution.

Table 1. The Composition of ATO surface (% wt) as function of Ar flash.

Time	Sn	O	Sb	C	Cl
20 min	38.8	56.4	1.8	1.1	1.9
0 min	25.0	55.9	1.2	16.1	1.9
2 min	29.1	57.3	1.6	9.9	2.2
5 min	32.8	57.6	1.7	5.6	2.3
15 min	37.7	56.6	1.8	2.3	1.6

If the surface of ATO coating is flashed by argon ions (2 keV), the carbon ion concentration decreases drastically, which fact confirms the supposition that this element is just a contamination issue (Table 2).
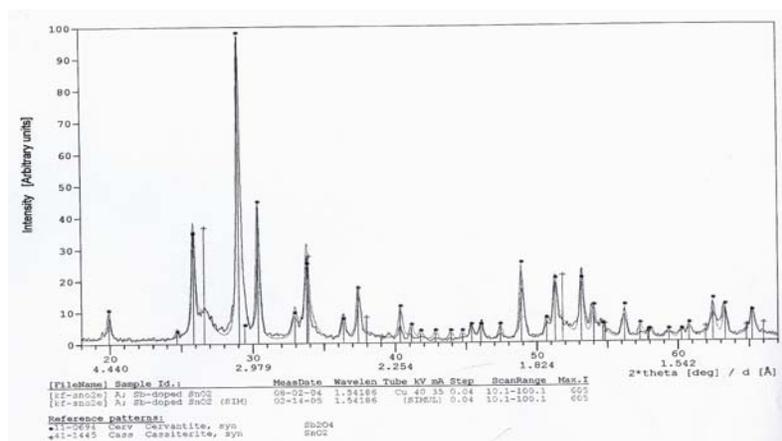

Fig. 3. XRD diagrams of ATO films produced by CVD.

XPS study also shows that in the range of 5 nm depth the composition of the film is constant.

Table 2. The composition of ATO surface (%wt) after argon flash.

Time	Sn	O	Sb	C	Cl
0 min	1.00	2.24	0.05	0.64	0.07
2 min	1.00	1.97	0.05	0.34	0.08
5 min	1.00	1.76	0.05	0.17	0.07
15 min	1.00	1.56	0.05	0.06	0.04
20 min	1.00	1.46	0.05	0.03	0.05

Based on these investigation it was confirmed that tin and antimony were found in the oxidation form SnO_2 and Sb_2O_5.

We were also interested in the analysis of the mechanical properties of ATO coatings. In this regard there were tested the hardness and elastic modulus of ATO films. In Table 3 it can be seen that the adhesion and the elastic modulus parameters of CVD samples are superior compared to the SG sample. SP coated sample has a much lower hardness (3.4 MPa) compared with CVD coatings (5.9 MPa). These low values can be attributed to the cracking of the layer.

Basically, these good mechanical properties of the ATO films are caused by the Si-O-Sn type bond that occurs between the film and the glass substrate and provides the remarkable wear resistance of these coatings.

Our major interest consists in the evaluation of electrical and optical properties of ATO films. In this direction we have investigated the sheet resistance, carrier number and transmittance in visible region for ATO coatings (Table 3).

It can be noticed that the CVD sample revealed a superior electrical conductivity compared with SG films. We can attribute this fact to the size of Sb ions with different oxidation number. Sb^{3+} ions are oxidized to Sb^{5+} ions and the radius of Sb^{5+} ions is smaller than that of Sn^{4+}

ions and it can easily replace the Sn^{4+} lattice sites. The defect formed by these replacements expulse electrons and behaves as a donor defect, in such way the number of current carriers is increased.

Table 3. The characteristics of ATO film obtained by different processes.

Film type	Particle size (nm)	Hardness (MPa)	Elasticity (MPa)	Sheet resistance (ohm/□)	Carrier number (cm^{-2})	Transmittance (%)
SG	190	3.4	32	220	4×10^{11}	82
CVD	328	5.9	73	38	1.7×10^{19}	78

The transmittance in visible region is almost the equal for the two types of ATO coatings: 82% for SG sample and 78% for CVD films (table 3).

We can conclude that ATO films prepared by CVD are superior to those prepared by sol-gel process. Despite the fact that sol-gel technique is a low cost preparing method, the practical applications require conductive ATO films with longer lifetime. These requirements are fulfilled by better adhesion and electrical conductivity of CVD samples.

Considering all the facts presented up to now in this work we focus the study on lifetime of ATO films prepared by CVD process. In this regard, the measurement of the anticorrosion behaviour of SnO_2:Sb films were made in different degrading medium.

The effect of the exposure of the ATO films to the influence of degrading medium is important, because the films have industrial applications: coating for architectural glass [7-8], bottle for wines[16], dimensional stable anodes [17-19].

A very convenient and precise way of evaluating the corrosion behaviour of a material in a given medium is the recording of a complete polarization curve under potentiodynamic control.

Table 4 show the evolution CVD films in different corrosive solutions (1M HCl, 1M NaCl and 1M tartric acid), during 1-120 days. The values of corrosion potential were recorded after 5 minutes of immersion in degrading medium.

Table 4. The corrosion evolution of CVD coatings.

Days	Corrosion Potential (mV)		
	HCl	NaOH	Tartric acid
1	138	184	102
3	137	184	102
5	138	184	103
7	138	185	101
10	137	183	102
20	137	183	101
30	135	182	101
60	133	180	98
120	130	175	94

It is observed that the presence of Sb:SnO_2 films deposited on glass lead to a very good protection against corrosion in all degrading media studied. The monthly corrosion rate is very low and the stability of the samples in all three chemical media is very good. The ATO films are stable during the first 30 days, and, after this time, it appears a slow degradation process.

The overall variation of the corrosion potential for ATO films compared to the sample, which is not exposed to the aggressive solution, is around 5-6 %.

The lifetime of CVD films was evaluated by monitoring the sheet resistance of the coating in the same degrading medium. The recorded values are presented in table 5

Table 5. The lifetime evolution of CVD coatings.

Days	Sheet resistance (ohm/□)		
	HCl	NaOH	Tartric acid
1	38	40	36
3	38	40	36
5	38	42	36
7	39	41	37
10	39	41	38
20	40	42	37
30	40	44	40
60	42	47	44
120	43	50	48

The variation of the sheet resistance for ATO films compared to the sample not exposed to the degrading medium is 20-30 %. For these films the best stability was found in HCl solution.

4. Conclusions

The mechanical and chemical stability of ATO SnO$_2$:Sb films are recognized but their lifetime is strongly dependent on the preparation conditions. The work reports on a study of the characteristics of ATO films deposited on the glass substrate by two different techniques (chemical vapour deposition and sol-gel method). The higher adhesion and electrical conductivity of the SG film warrant the stability of this type of films.

The investigations certified the SG technique, in challenge with the CVD, as a low-cost preparing method. Nevertheless, the applications in practice require conductive ATO films with long lifetime. CVD samples offer better adhesion and electrical conductivity.

The dependence of lifetime on the chemical medium was investigated by monitoring the evolution of sheet resistance and the corrosion potential during 120 days.

The ATO films are stable during the first 30 days. After this period of time it appears a slow degradation process.

Acknowledgement

References

[1] S. Saukko, V. Lantto, Thin Solid Films **436**, 137 (2003).
[2] I. B. Bernardi, L. E. Soledade, I. A. Santos, E. R. Leite, E. Longo, J. A. Varela, Thin Solid Films **405**, 228 (2002).
[3] K. D. Schierbaum, U. Weimar, W. Gopel, Sensors and Actuators **B7** (1/30), 709 (1992).
[4] B. Thangajaru, Thin Solid Films, **402**, 71 (2002).
[5] J. Puetz, F.N.Chalvet, M.A.Aegerter, Thin Solid Films **442**, 53 (2003).

114

[6] J. Szanyi, Applied Surface Science **185**, 161 (2002).

[7] A. P. Rizzato, L. Broussous, C.V. Santilli, S.H. Pulcinelli, A. F. Craievich,
Journal of Non-Crystalline Solids **284**, 61 (2001).

[8] J. Ma, X. Hao, X. Xu, Y. Yang, Sh. Huang, D. Zhang, C. Chen, Solid State
Communications **121**, 345 (2002).

[9] M. Guglieimi, Journal Sol-Gel Sci. Tech. **8**, 443 (1997).

[10] K. Nataka, Y. Morikawa, K. Yoshimura, H. Saito, Eur. Pat. Appl. EP1, **174**, 771 (2002).

[11] I. Kurisawa, M. Shiomi, S. Ohsumi, M. Tsubata, Journal of Power Source **95**, 125 (2001).

[12] Gy. Tolnai, F. Kormos, P. Nagy, E. Kálmán, Műszaki Szemle (2003), p.160-165

[13] P. M. Nagy, European Microscopy and Analysis 13-15 nov. 2004.

[14] P. Nagy, A. Csanády, E. Verő, G. Pálinkás, E. Kálmán, Mater. Sci. Forum **414-415**, 297
(2003).

[15] F. Kormos, L. Sziráki, I. Tarsiche, Laboratory Robotics Automation **24**, 291 (2000).

[16] M. Nakagawa, T. Amano, S. Yokokma, J. Non-Crystalline Solids **218**, 100 (1997).

[17] Y. Liu, Z. Li, Acta Materialia **52**, 721 (2004).

[18] E. Fockedey, A. Van Lierde, Water Research, **36**, 4169 (2002).

[19] H. M. Villulas, F. J. Mattos Costa, R. A. Nascemte, L. O.Bulhoes, Electrochimica Acta,
49, 3909 (2004).