ELSEVIER

Ceramics International 33 (2007) 625–629

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

# Preparation and properties of Sb-doped $SnO_2$/metal substrates by sol–gel and dip coating

M. Seo [*], Y. Akutsu, H. Kagemoto

*Department of Environmental Studies, Graduate School of Frontier Sciences, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*

Received 20 September 2005; received in revised form 14 October 2005; accepted 7 November 2005

## Abstract

Antimony-doped $SnO_2$ on metallic substrate is a useful electrode for electrochemical water treatment system. The Sb-doped $SnO_2$ films on aluminum and stainless steels, which are relatively workable or available metals, were prepared by the sol–gel technique and dip coating method. The precursor metal alkoxide/alcohol solutions were derived from $SnCl_4$ and $SbCl_3$. Ammonia/alcohol solution was used for the synthesis and $Cl^-$ was eliminated by the precipitation of $NH_4Cl$. The X-ray diffraction pattern of the $SnO_2$ film annealed at 400 °C could be assigned to $SnO_2$. The Sb-$SnO_2$ film consisted of fine particles from 10 to 20 nm. In the electrolysis, Sb-$SnO_2$/stainless steel electrodes showed an exfoliation but Sb-$SnO_2$/aluminium did not. Our results indicate that $SnO_2$/Al can be promising as a $SnO_2$ electrode for electrochemical water treatment.

*Keywords:* A. Sol–gel processes; E. Substrates; E. Electrodes; Sb-doped tin oxide

## 1. Introduction

Tin dioxide is transparent in the visible-light region, and chemically and thermally stable. It shows a high electrical conductivity in the presence of dopants; therefore, it has been used as displays, heat shields, transparent electrodes, gas sensors [1–4], etc.

Furthermore, $SnO_2$ is also useful for water treatment [5–8]. When electrolysis in water is performed with anodes of (antimony or fluorine)-doped $SnO_2$ thin films prepared on titanium substrates, hydroxyl radical—a strong oxidant—is efficiently generated on the surface of the $SnO_2$ thin film. Thereby, these $SnO_2$/metal electrodes can be used for the electrochemical advanced oxidation process (EAOP)—one of the water treatment methods that decompose persistent organic pollutants [8,9].

On the EAOP water treatment, since hydroxyl radicals are generated on the surface of electrode, it is desirable that large amount of pollutant components in the water can directly touch the surface of electrode; therefore, size and shape of the electrode or its position in an electrolysis cell also affects an efficiency of water treatment. In order to fabricate more efficient EAOP system, we should consider the way of electrolysis, and examine not only properties of electrodes but also their shape and size.

Many results of wastewater treatment or decomposition of specific compounds using $SnO_2$/Ti electrodes, which are $SnO_2$ thin films on titanium substrates with the simple shape such as sheet, bar or mesh, have been reported. Nevertheless, few studies, which are concerned with $SnO_2$ electrode having complex shape or non-titanium substrate, have been found [10]. This is presumed owing to largely two reasons, (1) it is mainly focused on materials of electrode, decomposition efficiency or mechanism about degradation of many pollutants with simple shape electrodes, (2) titanium has been found to be suitable for substrate because it is a superior metal for chemicals and heat, on the other hand, it is hard to prepare various shape of titanium substrate, because titanium is poorly workable, more expensive and less available than common metals such as aluminum or iron. As a result, it is difficult to make a $SnO_2$ coated electrode for considering and devising a different water treatment system.

Tin dioxide thin films have been prepared on silicon, glass, or titanium substrate using various techniques such as chemical vapor deposition [11], sputtering [12], spray pyrolysis [13], etc. These techniques, however, have some limitations in size,

---

[*] Corresponding author. Tel.: +81 3 58416545; fax: +81 3 38158360.
*E-mail addresses:* seo@yuiko.t.u-tokyo.ac.jp (M. Seo), acts@k.u-tokyo.ac.jp (Y. Akutsu).

0272-8842/$32.00 © 2006 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2005.11.013

shape and properties of the substrates. In addition, special facilities and a great deal of materials are needed, thus, it is difficult to form $SnO_2$ thin films on a substrate with complex shape. The sol–gel technique is one of the attractive methods to coat wide substrates with a $SnO_2$ thin film using simple equipment, and the dip coating method is suitable for coating a substrate having various shapes. For example, it is expected to form $SnO_2$ film inside the thin pipe by sol–gel technique and dip coating method.

Metal alkoxides are suitable materials for the sol–gel technique, but commercial Sn alkoxides are very expensive; therefore, it is helpful to synthesize them from tin chlorides in order to prepare a large amount of Sn alkoxides at a lower cost. In this case, it is a basic solution when tin chloride is dissolved in an alcohol, and this solution which contains much $Cl^-$ or $H^+$ is used to form $SnO_2$ thin film [14]. There is no problem to directly soak glass, silicon or titanium substrates in the solution, but common metals or alloy substrates, like aluminum or stainless steels, cannot be used in the solution owing to the corrosion by $Cl^-$ and $H^+$. Therefore, removal of these ions from the solution is indispensable procedure at least for these metals.

However, these common metals or alloys have excellent advantages—more workable, reasonable in price and available than titanium. If these metals and cheaper materials such as tin chloride can be used and only the simple procedure is needed, $SnO_2$ electrodes of various sizes and shapes can be easily prepared. With various $SnO_2$ electrodes, it is expected that we can consider and devise much superior system for water treatment.

Needless to say, many articles have described the preparations and properties of a $SnO_2$ thin film [14–19], but we were not able to find studies for preparing a $SnO_2$ film on common metals or alloy substrates by the sol–gel technique and dip coating method. We prepared the $SnO_2$/metal (aluminum and stainless steel) by these methods. This paper reports the process of a simple preparation technique for the precursor sol solution derived from $SnCl_4$, which can be used on aluminum and stainless steel substrates, and the properties of the Sb-doped $SnO_2$ thin film which was prepared using the sol solution. Furthermore, the possibility of $SnO_2$ coated on these metals as electrodes for wastewater treatment is discussed by an electrolysis in the water containing *N*,*N*-dimethyl-*p*-nitrosoaniline which can selectively trap hydroxyl radicals [20].

## 2. Experimental procedures

### 2.1. Preparation of sol solution and $SnO_2$/metal substrate

Ammonia/alcohol solutions were made by injecting $NH_3$ (gas) into ethanol or 1-propanol. Ammonia/ethanol was slowly added to a 1 M $SnCl_4$ ethanol solution until the pH ranged between 8.2 and 8.4, and then ethanol was added to the mixed solution to produce the theoretical concentration of 0.3 M tin ethoxide. In the mixed solution, $NH_4Cl$ (poor solubility in ethanol) was produced due to the reaction of $Cl^-$, $H^+$ and $NH_3$. After the separation and removal of $NH_4Cl$ using a centrifuge, the supernatant solution was placed in a freezer for 2 days at −18 °C. A small amount of $NH_4Cl$ was deposited to the bottom of the vial due to decline of the solubility by cooling, and only the solution was decanted to another vial. In the same way, a 1-propanol solution with the theoretical concentration of 0.15 M antimony propoxide was synthesized from 0.5 M $SbCl_3$ 1-propanol solution, $NH_3$/1-propanol and 1-propanol.

The sol solution for the Sb-doped $SnO_2$ was prepared as follows: first, Sn ethoxide/ethanol was added to ethanol solution and then Sb propoxide/1-propanol was mixed with [Sb] concentration in a proportion of 5%. [Sb] content was estimated by EDXRF (JEOL JSX-3220). Next, the 1-propanol containing $H_2O$ (propanol:$H_2O$ = 9:1 by volume) was slowly added to the Sn ethoxide/ethanol solution with ultrasonic irradiation, and then ethylene glycol containing ethanol (ethylene glycol:ethanol = 9:1 by volume) was added to the mixed solution and then it was shaken thoroughly. Finally, it was exposed to ultrasonic irradiation for 15 min again. Total volume ratio of Sn ethoxide/ethanol solution in the sol solution was 60%, Sb propoxide/propanol solution was 12%, and pure ethylene glycol was 7.2%. On the other hand, the sol solution for the pure $SnO_2$ was prepared in the same way without the addition of the Sb propoxide/1-propanol.

We used sheet substrates (1.5 cm × 5 cm) of aluminum, stainless steels (austenitic SUS316, 18Cr–8Ni–2.5Mo–Fe balance; ferritic SUS430, 17Cr–Fe balance), glass and titanium. These substrates were washed using a detergent, and all substrates were rinsed with distilled water. These washed substrates were soaked in acetone, and then they were exposed to the ultrasonic irradiation for 15 min. Finally, all the substrates were thoroughly washed with distilled water and dried again. These substrates were soaked in the sol solution, and then withdrawn at the rate of 3 cm $min^{-1}$. They were dried at room temperature for 10–15 min. These dried substrates were placed in a furnace, dried at 150 °C for 20 min, and then annealed at 400 °C for 60 min to form the $SnO_2$ thin film. This series of coating and annealing processes was repeated 20 times.

All of the processes were conducted under atmospheric conditions, below 40% humidity and room temperature at about 20 °C.

### 2.2. Measurement

The X-ray diffraction measurement was carried out using a RIGAKU Mini Flex, with Cu Kα radiation. The structure of the $SnO_2$ thin film surface was examined by SEM (HITACHI S-900); at the same time, the thickness of the film was measured with a fractured surface of $SnO_2$/glass. The hardness and exfoliation of $SnO_2$ thin film were examined by a scratch test (pencil hardness: HB, F, H, 2H, 3H, 4H, 5H, 6H, 7H, 8H, 9H where 9H is the hardest) and an adhesion tape test. The sheet resistivity was estimated at room temperature by the four-point probe technique [21].

Tin dioxide/metal substrates ($SnO_2$/Al, $SnO_2$/SUS316, $SnO_2$/SUS430 and $SnO_2$/Ti) with areas of 12 $cm^2$ (1.5 cm × 4 cm) were used as anodes and the same size SUS316 sheet was used as the cathode. The *N*,*N*-dimethyl-*p*-

nitrosoaniline (RNO) can selectively trap OH radicals. This RNO has a large absorption coefficient at 440 nm, and the OH-trapped RNO does not absorb light at this wavelength; therefore, it is easy to monitor this change [8,20]. It is detected with spectrophotometer (Hitachi U-2800). Two electrodes (anode and cathode) were placed facing each other in a 45 ml of 0.1 M phosphate buffer solution containing 0.02 mM RNO, and a 12 mA current was passed for 30 min with stirring.

## 3. Results and discussion

The reaction of the synthesis of a tin alkoxide, in which amine is used, is as follows [14]:

$$\mathrm{SnCl_4 + 4\,ROH + 4\,amine \rightarrow Sn(OR)_4 + 4\,amine \cdot HCl}$$

In this study, ammonia was used instead of amine, because ammonia has the lower boiling point, and it can be easily removed on drying or annealing after dip coating, even if additional ammonia is contained in the sol solution. Ammonia was provided as ammonia/alcoholic solution, in which ammonia gas was bubbled into a pure alcohol beforehand, and it was added to the tin chloride alcoholic solution, in order to prevent intense release of heat of reaction and easily adjust pH.

The 3 ml of synthetic tin ethoxide/ethanol solution was dried, and heated at 1000 °C under atmospheric condition, and then Sn oxidized into $SnO_2$, which was identified by XRD. Tin concentration in the solution was estimated as 0.3 M from the weight measurement of $SnO_2$.

Generally, if a sol solution containing metal alkoxide is used under air condition, it gets quickly clouded by the undesirable reaction due to mixing of $H_2O$ in the air. However, the sol solution which contained ethylene glycol kept transparent much longer than the solution without ethylene glycol.

The tin dioxide films formed on the glass and stainless steels by this sol–gel technique and dip coating method were flat and smooth. The films on aluminum were also flat, but they looked a little rough. They showed different colors, i.e. transparent (non-doped) and light grey (5% Sb-doped). On the other hand, no difference in the film colors on the stainless steels and titanium was observed since these substrates themselves remarkably changed colors by heating at 400 °C. The exfoliation of $SnO_2$ from substrate by an adhesive tape did not occur, and the $SnO_2$ film had over 9H pencil hardness. The sheet resistivity of the $SnO_2$ thin film was estimated to be 1.16 kΩ/sq. (5% Sb-doped) and over 100 kΩ/sq. (non-doped) using $SnO_2$ on glass which is a nonconductive substrate.

The XRD measurements were conducted for (Sb-doped, non-doped) $SnO_2$/glass, and $SnO_2$/Al which had the largest coefficient of thermal expansion among the metal substrates used in this study. The XRD patterns of these samples are shown in Fig. 1. Although the diffraction peaks are not sharp, the pattern can be easily assigned to the $SnO_2$ structure, meanwhile, no peaks for antimony oxides were observed. However, comparing the Sb-doped sample with the non-doped one on each substrate, the diffraction peaks become broader when containing Sb. It is suggested that the antimony oxide phases have mixed with the $SnO_2$ structure.

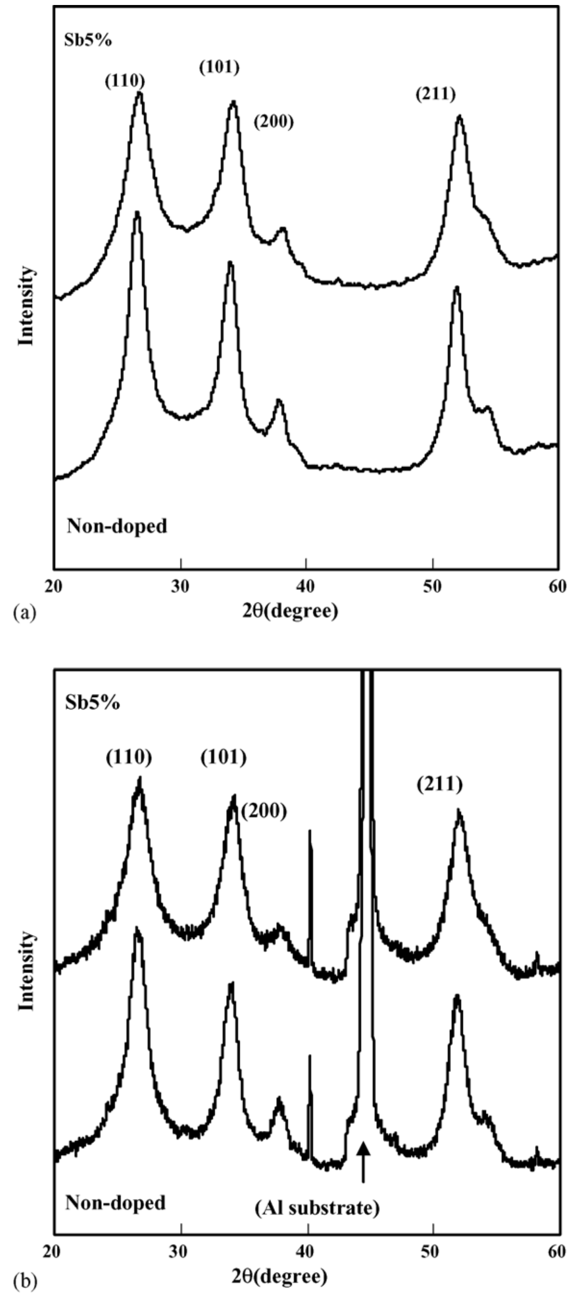

Fig. 1. XRD patterns of (Sb-doped or non-dopned) $SnO_2$ film on glass (a) and on aluminum (b).

Fig. 2 shows the surface of the Sb-$SnO_2$/stainless steel SUS316. The tin oxide film was composed of fine particles of 10–20 nm. The Sb-$SnO_2$ film on the substrate did not have cracked after 20 times dip coating, and the other samples by 20 times coating had a similar appearance. However, for 10 times dip coating, some cracks appeared on the surface of the Sb-$SnO_2$ film on the aluminum and stainless steels, on the other hand, not on glass and titanium. This is presumably caused by the difference in the coefficients of thermal expansion of these substrates.

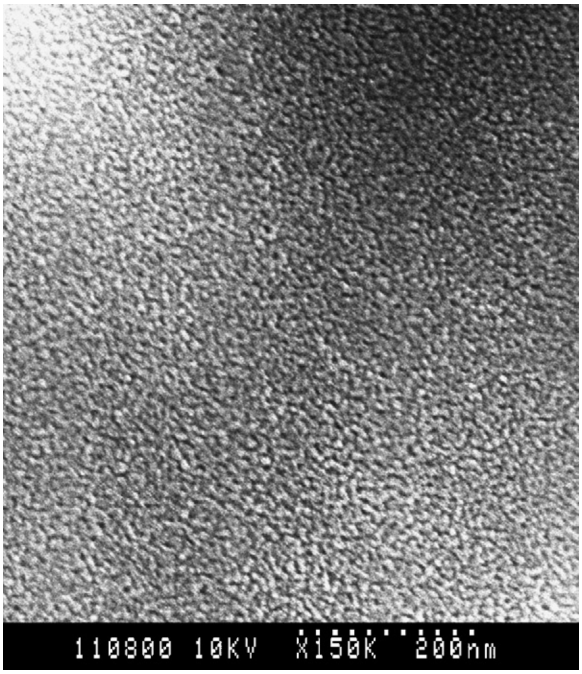

Fig. 2. SEM photograph of the surface of $SnO_2$ film on SUS316 after 20 times coating.

A fractured surface of the Sb-$SnO_2$/glass is shown in Fig. 3. The thickness of Sb-$SnO_2$ film measured about 850 nm. This thickness can be applied to all samples, because the Sb-$SnO_2$ film formed by one process cycle is very thin (30–50 nm); therefore, the final thickness approximates the value obtained by the 20 times coating process, even if the thickness was different for the several initial coating processes due to the surface condition of each substrate.

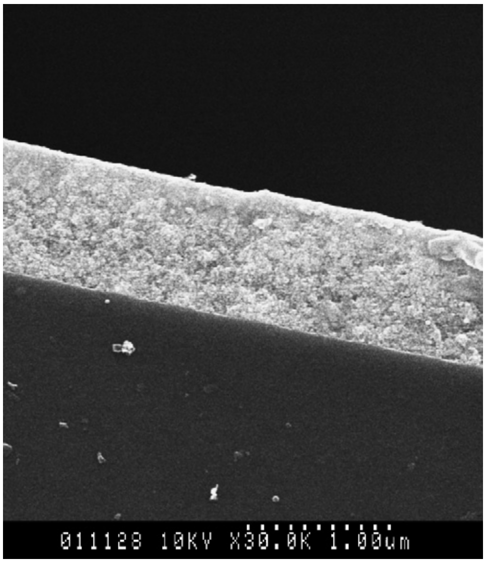

Fig. 3. SEM photograph of the fractured surface of $SnO_2$ film on glass.

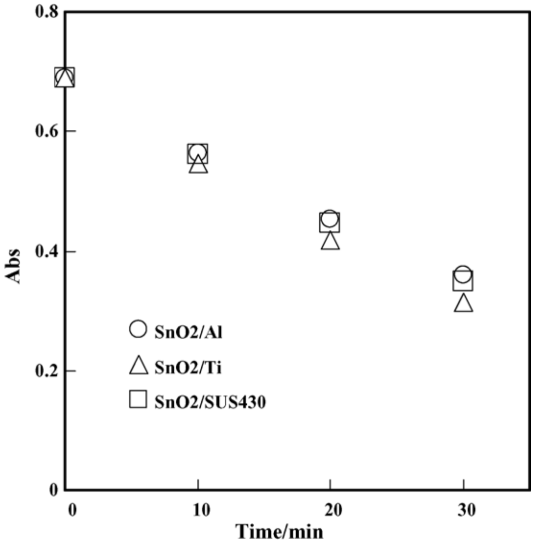

Fig. 4. The change in absorbance of 0.2 mM RNO solution obtained at maximum absorption wavelength during 30 min electrolysis with different anodes.

Fig. 4 shows the absorbance obtained at the maximum absorption wavelength of RNO during the electrolysis for 30 min in 0.2 mM RNO aqueous solution. If the absorbance of RNO decreases with the electrolysis time, it indicates that OH radicals are generated by the electrolysis of water and trapped by RNO. When the electrolysis with Sb-$SnO_2$/metal anodes in water containing RNO was performed, Sb-$SnO_2$ on SUS316 remarkably came off the substrate; therefore, the result of the Sb-$SnO_2$/SUS316 was excluded. Hydroxyl radicals were generated to the same degree for three Sb-$SnO_2$/metal anodes.

After electrolysis, only a little exfoliation of the Sb-$SnO_2$ film was observed on Sb-$SnO_2$/SUS430, but not on Sb-$SnO_2$/Al and Sb-$SnO_2$/Ti. Furthermore, when the electrolysis was conducted over 30 min, the exfoliation of the Sb-$SnO_2$ film on Sb-$SnO_2$/SUS430 eventually expanded and the OH radical generation decreased.

Considering the exfoliations of Sb-$SnO_2$ on SUS316 and SUS430, it was assumed that the Sb-$SnO_2$ film combined weakly with the stainless steel substrates. During electrolysis of water, $O_2$ gas was also generated on the anode ($SnO_2$ electrode), on which the gas could be observed as bubbles, and it is more easily generated on stainless steels than on Sb-$SnO_2$. Therefore, it is supposed that water and the metal substrate directly touched through a part of frail bond between particles of $SnO_2$ on Sb-$SnO_2$ film, and then the Sb-$SnO_2$ film was pushed up by the pressure of generated $O_2$ bubbles and came off the substrate, or the substrate itself dissolved in the water as a metallic ion.

In addition, hydroxyl radicals were hardly generated by metal electrodes such as metal substrates used in this experiment. Therefore, it was suggested that the decrease of OH radical generation by Sb-$SnO_2$/SUS was caused by the increasing part of metal substrate directly exposed to water due to the exfoliation of the Sb-$SnO_2$ thin film.

It is assumed that an exfoliation of the Sb-$SnO_2$ film on the aluminum might exist because aluminum has a larger coefficient of thermal expansion than SUS316 or SUS430. The exfoliation of Sb-$SnO_2$/Al, however, could not be observed and hydroxyl radicals were constantly generated. It is presumed that aluminum generated less $O_2$ than iron (stainless steels), and the Sb-$SnO_2$ film could remain on the aluminum during the electrolysis. Moreover, Sb-$SnO_2$/Al electrode had almost similar effect to Sb-$SnO_2$/Ti under this experimental condition. Therefore, Sb-$SnO_2$/Al is a promising material as a Sb-$SnO_2$ electrode for electrochemical water treatment.

## 4. Conclusions

Antimony-doped $SnO_2$ thin films on more workable or available metal substrates than titanium were prepared by the simple procedure of the sol–gel technique and dip coating method. The precursor Sn ethoxide was synthesized from $SnCl_4$ in ethanol using $NH_3$/ethanol solution, and $Cl^-$ was eliminated by the precipitation of $NH_4Cl$. Sb propoxide was synthesized in the same way from $SbCl_3$ using 1-propanol and $NH_3$/1-propanol solution. The sol solution for the dip coating containing these alkoxides and ethylene glycol allowed preparing a Sb-$SnO_2$ thin film on reasonable metal substrates under atmospheric conditions. The X-ray diffraction pattern of the thin film, which was annealed at 400 °C, corresponded to Sb-$SnO_2$, and no crack was found in the thin film on the metal substrates after 20 times dip coating. When Sb-$SnO_2$/stainless steel substrates were used as electrodes for the electrolysis in water, the Sb-$SnO_2$ film came off the substrates. This suggests that the bonding strength between the Sb-$SnO_2$ film and stainless steel substrates is weak and parts of the substrate are in direct contact with water. The Sb-$SnO_2$/Al electrode, however, can be used in water because of rather strong bonding between the film and the substrate, and it is expected to be a useful material when considering an electrolysis system.

## References

[1] J. Puetz, M.A. Aegerter, Sol–gel coating of thin display glasses—problems and remedy, J. Sol–Gel Sci. Technol. 32 (2004) 125–129.

[2] C.G. Granqvist, Window coating for the future, Thin Solid Films 193/194 (1990) 730–741.

[3] S. Ito, Y. Makari, T. Kitamura, Y. Wada, S. Yanagida, Fabrication and characterization of mesoporous $SnO_2$/ZnO–composite electrodes for efficient dye solar cells, J. Mater. Chem. 14 (2004) 385–390.

[4] A. Teeramongkonrasmee, M. Sriyudthsak, Methanol and ammonia sensing characteristics of sol–gel derived thin film gas sensor, Sens. Actuat. B 66 (2000) 256–259.

[5] S. Tanaka, Y. Nakata, T. Kimura, Yustiawati, M. Kawasaki, H. Kuramitz, Electrochemical decomposition of bisphenol A using Pt/Ti and $SnO_2$/Ti anodes, J. Appl. Electrochem. 32 (2002) 197–201.

[6] Y.J. Feng, X.Y. Li, Electro-catalytic oxidation of phenol on several metal-oxide electrodes in aqueous solution, Water Res. 37 (2003) 2399–2407.

[7] M. Panizza, C. Bocca, G. Cerisola, Electrochemical treatment of wastewater containing polyaromatic organic pollutants, Water Res. 9 (2000) 2601–2605.

[8] C. Comninellis, Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for waste water treatment, Electrochim. Acta 39 (1994) 1857–1862.

[9] I. Tröster, M. Fryda, D. Herrmann, L. Schäfer, W. Hänni, A. Perret, M. Blaschke, A. Kraft, M. Stadelmann, Electrochemical advanced oxidation process for water treatment using DiaChem® electrodes, Diamond Relat. Mater. 11 (2002) 640–645.

[10] J. Santos-Peña, T. Brousse, L. Sánchez, J. Morales, D.M. Schleich, Antimony doping effect on the electrochemical behavior of $SnO_2$ thin film electrodes, J. Power Sources 97/98 (2001) 232–234.

[11] S.C. Ray, M.K. Karanjai, D. Dasgupta, Preparation and study of doped and undoped tin dioxide films by the open air chemical vapour deposition technique, Thin Solid Films 307 (1997) 221–227.

[12] N.Y. Shishkin, I.M. Zharsky, V.G. Lugin, V.G. Zarapin, Air sensitive tin dioxide thin films by magnetron sputtering and thermal oxidation technique, Sens. Actuat. B 48 (1998) 403–408.

[13] J. Peña, J. Pérez-Pariente, M. Vallet-Regí, Textural properties of nanocrystalline tin oxide obtained by spray pyrolysis, J. Mater. Chem. 13 (2003) 2290–2296.

[14] M. Epifani, M. ALvisi, L. Mirenghi, Sol–gel processing and characterization of pure and metal-doped $SnO_2$ thin films, J. Am. Ceram. Soc. 84 (2001) 48–54.

[15] C. Terrier, J.P. Chatelon, J.A. Roger, R. Berjoan, C. Dubois, Analysis of antimony doping in tin oxide thin films obtained by the sol–gel method, J. Sol–Gel Sci. Technol. 10 (1997) 75–81.

[16] J.C. Giuntine, W. Granier, J.V. Zanchetta, A. Taha, Sol–gel preparation and transport properties of a tin oxide, J. Mater. Sci. Lett. 9 (1990) 1383–1388.

[17] B. Canut, V. Teodorescu, J.A. Roger, M.G. Blanchin, K. Daoudi, C. Sandu, Radiation-induced densification of sol–gel $SnO_2$: Sb films, Nucl. Instrum. Methods Phys. Res. B 191 (2002) 783–788.

[18] J.P. Chatelon, C. Terrier, E. Bernstein, R. Berjoan, J.A. Roger, Morphology of $SnO_2$ thin films obtained by sol–gel technique, Thin Solid Films 247 (1994) 162–168.

[19] M.A. Dal Santos, A.C. Antunes, C. Ribeiro, C.P.F. Borges, S.R.M. Antunes, A.J. Zara, S.A. Pianaro, Electric and morphologic properties of $SnO_2$ films prepared by modified sol–gel process, Mater. Lett. 57 (2003) 4378–4381.

[20] D. Wabner, C. Grambow, Reactive intermediates during oxidation of water at lead dioxide and platinum electrodes, J. Electroanal. Chem. 195 (1985) 95–108.

[21] S. Murashima, H. Kanamori, F. Ishibashi, Correction devisors for the four-point probe resistivity measurement on cylindrical semiconductor, Jpn. J. Appl. Phys. 9 (1970) 58–67.