Journal of Alloys and Compounds 489 (2010) 257–261

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Thin nanocrystalline TiO_2–SnO_2 sprayed films: Influence of the dopant concentration, substrate and thermal treatment on the phase composition and crystallites sizes

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ARTICLE INFO

Article history:
Received 25 May 2009
Received in revised form
11 September 2009
Accepted 14 September 2009
Available online 23 September 2009

Keywords:
Thin films
Nanostructured materials
X-ray diffraction

ABSTRACT

Thin nanocrystalline TiO_2–SnO_2 films (0–50 mol% SnO_2) are coated on quartz and stainless steel substrates by spray pyrolysis method. The synthesized films are investigated by XRD, Raman spectroscopy and XPS.

The diffraction peaks of anatase phase fade while the peaks of rutile phase appear in the X-ray profiles with increasing of the treatment temperature and the content of SnO_2 in the sprayed films. It is found that SiO_2 coming from the quartz substrate stabilizes the anatase phase up to 700 °C. A more pronounced crystallization of rutile is registered with the films deposited on stainless steel substrate, which probably is caused by combined effect of SnO_2 doping and penetration of iron and chromium from the substrate inside the films.

Dopant concentration (SnO_2) influences the size of the crystallites of the titania films deposited on quartz substrates The size of crystallites in the titania films decreases from 45 to 25 nm with increasing of SnO_2 amount.

The SnO_2 amount does not affects substantially the size of crystallites (about 23 nm) for the films deposited on stainless steel.

1. Introduction

During the recent years the interest in titania thin films has considerably increased due to a variety of useful properties and applications [1–6]. Only few papers are dedicated to the investigation of SnO_2 doped titania films as photocatalysts [7–9] and gas sensors [10–13]. Moreover, there is a discrepancy in the literature about the crystalline stability of TiO_2/SnO_2 system. It is claimed that the tin oxide in TiO_2/SnO_2 binary oxides stabilizes the anatase phase [7,14,15]. In contrast, other authors prove that the tin promotes the phase transformation from anatase to rutile and forms a solid solution with TiO_2 [12,16,17] The data about the effect of the type of substrate used on the phase composition and crystallite size of TiO_2 films are scarce in the accessible literature. The investigations, concerning titania films deposited on stainless steel substrates, could be of significant importance due to the possible applications of them as photocatalytic electrodes [18] and anticorrosion coatings [19]. Nevertheless there is a lack of systematic studies dealing with the phase composition and microstructure (the crystallites size) of TiO_2 and TiO_2–SnO_2 films deposited on steel substrate.

The aim of this paper is to investigate the effect of thermal treatment temperature, type of substrate and concentration of tin dioxide on the anatase phase stability and the size of the crystallites of TiO_2–SnO_2 sprayed films.

2. Experimental

For the spray pyrolysis, 0.2 M precursor solutions of $TiCl_4$ and $SnCl_4$ in ethanol were prepared. The final spraying solutions contain 0–50 mol% SnO_2 in order to obtain different amounts of SnO_2 in the sprayed films.

The solutions were sprayed onto the substrates heated up a temperature from 300 to 450 °C. The spray coating was carried out at a 10-s interval between the sprays in order to keep the substrate temperature nearly constant. The thickness of films obtained was about 200 nm. A full decomposition of the precursors and crystallization of the films were achieved after treatment of the samples at different temperatures in the range of 500–800 °C for 60 min in air.

The quartz and stainless steel substrates were cleaned successively in hot ethanol and acetone.

The crystalline phase composition of samples was studied by X-ray diffraction (XRD) using a X-ray diffractometer Philips PW 1050 with CuKα-radiation. X-ray diffraction-line broadening (XRD-LB) measurements were carried out in order to estimate the crystallite size. The composition and electronic properties of the titania layers were investigated by X-ray photoelectron spectroscopy (XPS). The measurements were performed in a VG ESCALAB II electron spectrometer using AlKα radiation with an energy of 1486.6 eV.

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0925-8388/$ – see front matter
doi:10.1016/j.jallcom.2009.09.066

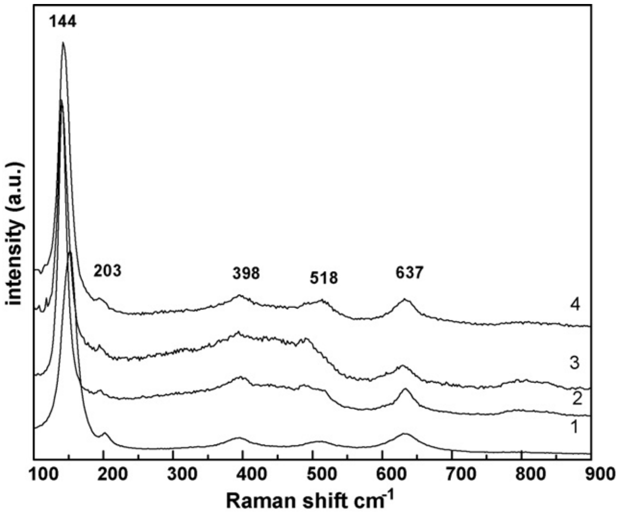

Fig. 1. Raman spectra of TiO_2–SnO_2 thin films, treated at 500 °C: (1) TiO_2, (2) TiO_2–1 mol% SnO_2, (3) TiO_2–5 mol% SnO_2 and (4) TiO_2–15 mol% SnO_2.

3. Results and discussion

The phase composition of tin doped titania films were investigated by XRD and Raman spectroscopy. In some cases the Raman spectroscopy is a more powerful method for titania phase identification than the XRD analysis due to high sensitivity.

The Raman spectrum of an undoped TiO_2 thin film deposited on quartz substrate and annealed at 500 °C shows the formation of anatase (Fig. 1) in contrast to the XRD analysis of the films, which indicates only amorphous hallo. We find amorphous also the XRD profiles of sprayed pure SnO_2 thin films on quartz substrate, heated at 500 °C. On the other hand, SnO_2 doped titania films (1–20 mol%) annealed at temperatures 500–700 °C and pure TiO_2 annealed at 600–700 °C contain only anatase phase (A). A rutile phase (R) appears only in the TiO_2 films doped with 50 mol% SnO_2 annealed at 600 °C (Fig. 2). The broad anatase peak, registered for TiO_2–SnO_2 (50 mol%) films (Fig. 2f), consists of two phases: anatase and a nonstoichiometric Ti_3O_5 phase (T). For these samples the Raman analysis confirms the results obtained by X-ray diffraction.

The diffraction peaks from rutile crystallites appear in the X-ray profiles with increasing of the content of SnO_2 in the films. The addition of SnO_2 has a promoting effect on the transformation anatase to rutile crystalline phase [12,16,20], due to the rutile like structure of SnO_2-cassiterite phase.

The XRD-LB measurements show that the samples obtained after annealing at 500–700 °C possess typical nanocrystalline dimensions of 20–45 nm (Table 1). Obviously, the increase of SnO_2 content results in a slight decrease in the crystalline dimensions. It is found also (Fig. 2) that the peak position of (1 0 1) anatase shifts

Table 1
The size of anatase crystallites in TiO_2–SnO_2 sprayed films after thermal treatment at 500 °C, evaluated by Scherrer's formula.

Sample mol% SnO_2	Crystalline size for films deposited on quartz substrate (nm)	Crystalline size for films deposited on stainless steel substrate (nm)
0	Amorphous	24
1	45	23
3	38	23
5	33	23
10	31	22
15	28	22
20	26	23
50	25	22

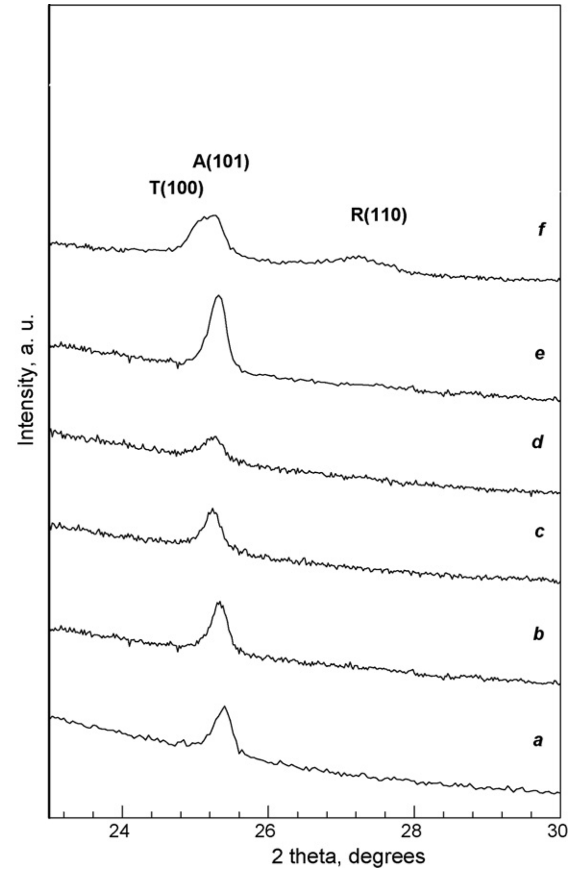

Fig. 2. XRD spectra of sprayed TiO_2 films doped with different SnO_2 content, annealed at 600 °C on quartz substrates: (a) 0 mol%, (b) 1 mol%, (c) 5 mol%, (d) 15 mol%, (e) 20 mol% and (f) 50 mol%.

to a smaller scattering angle side with increasing of the SnO_2 content in TiO_2 films. This may come from the exchange of Ti with Sn in the anatase phase crystallites. Formation of a solid solution in the TiO_2–SnO_2 system is observed for the samples containing 1–15 mol% SnO_2 The interplanar distance, d_{101}, gradually changes from 3.507 Å (for the pure TiO_2 films) to 3.525 Å (for films with 15 mol% SnO_2). The same values for d_{101} are calculated by Martinez et al. [9]. The reason for formation of solid solution is the discrepancy between the two ionic radii: Ti^{4+} (0.068 Å) and Sn^{4+} (0.071 Å). The difference of about 4.23% is sufficient to cause the observed deviation in *d* values. [13].

The investigations of chemical composition by XPS shows the presence of 3.5 and 5.6 at.% Si in pure TiO_2 films annealed at 500 and 600 °C, respectively. This could be explained by interaction of quartz substrate with the films similarly to the sprayed ZrO_2 films [21]. From these results, inclusion of the SiO_2 in TiO_2 films may stabilize the anatase phase. This suggestion is in accordance with the results obtained by Yoshinaka et al., who indicates that the addition of only 5 mol% SiO_2 to TiO_2 has a retarding effect on the anatase–rutile transformation [22]. Also Nikolic et al. [23] have found that the transformation rate of TiO_2 sol–gel films is lower on quartz and single crystal quartz than on alumina substrate.

The undoped TiO_2 thin films, deposited on stainless steel and annealed at 500 °C, contain only anatase phase, while the undoped TiO_2 annealed at 600 °C include also small quantity of rutile, as shown in Fig. 3. The TiO_2 films, doped with 3–20 mol% SnO_2 and heated in the temperature range 500–700 °C, consist of anatase crystallites as the main phase and rutile crystallites. It is also found that the share of rutile crystallites increases, when the SnO_2 content in the films increases. The transformation anatase–rutile started at

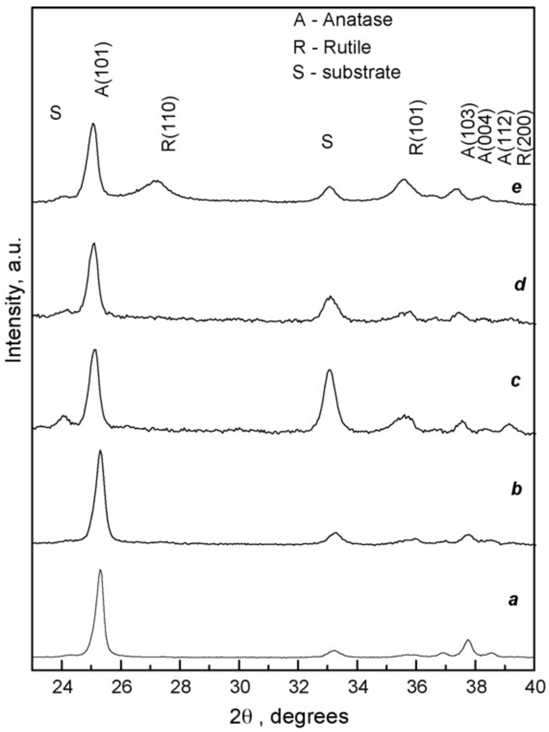

Fig. 3. XRD spectra of sprayed TiO_2 films doped with different SnO_2 content, annealed at 600 °C on stainless steel: (a) 0 mol%, (b) 3 mol%, (c) 10 mol%, (d) 20 mol% and (e) 50 mol%.

500 °C for the sample doped with 50 mol% SnO_2; after annealing at 700 °C, almost the same peak height of rutile phase as that of anatase phase is observed in contrast to the phase composition of the films deposited on quartz substrate (Fig. 4).

According to Zhang and Banfield [24], the phase transition to rutile depends on the grain size: rutile is the most stable phase when the grain size is greater than 35 nm. Our results differ from this data as tin doped titania films contain crystallites considerably smaller than 35 nm (Table 1). Consequently, in our case the chemical composition of sprayed titania films has a more pronounced effect on the rutile crystallization than the size of the crystallites. The chemical composition of TiO_2 film deposited on stainless steel substrates is investigated by X-ray photoelectron spectroscopy, which indicates some interaction between the substrate and the film similar to the case of tin doped titania deposited on quartz substrate.

It has been proven that the sprayed TiO_2–SnO_2 films (0–50 mol%) annealed at 500 °C contain 3 at.% iron, while the concentration of iron is 4 at.% in the films annealed at 700 °C. The strong promoting effect of iron addition to titania on the anatase–rutile transition has been established by several authors [27–29]. Zhang et al. revealed that the dopant Fe_2O_3 decreases the phase transition temperature of TiO_2 powder samples [28]. The thermal treatment causes a more pronounced diffusion of chromium from the steel substrate to the films than that of the iron. The concentration of chromium in the titania films, annealed at 500 °C, is 2.6 at.% and the treatment at 700 °C results in an increase of the Cr concentration up to 5.9 at.% (Fig. 5). According to the investigations of MacKenzie, the addition of 1 mol% Cr into titania powder leads also to appearance of 9% rutile phase after thermal treatment [27].

The introduction of SnO_2, as a dopant, probably promotes also the formation of rutile due to the fact that cassiterite and rutile have identical crystal structures [16]. In our samples treated at 700 °C, the presence of significant quantity of rutile phase could be explained by the combining effect of Sn dopant as

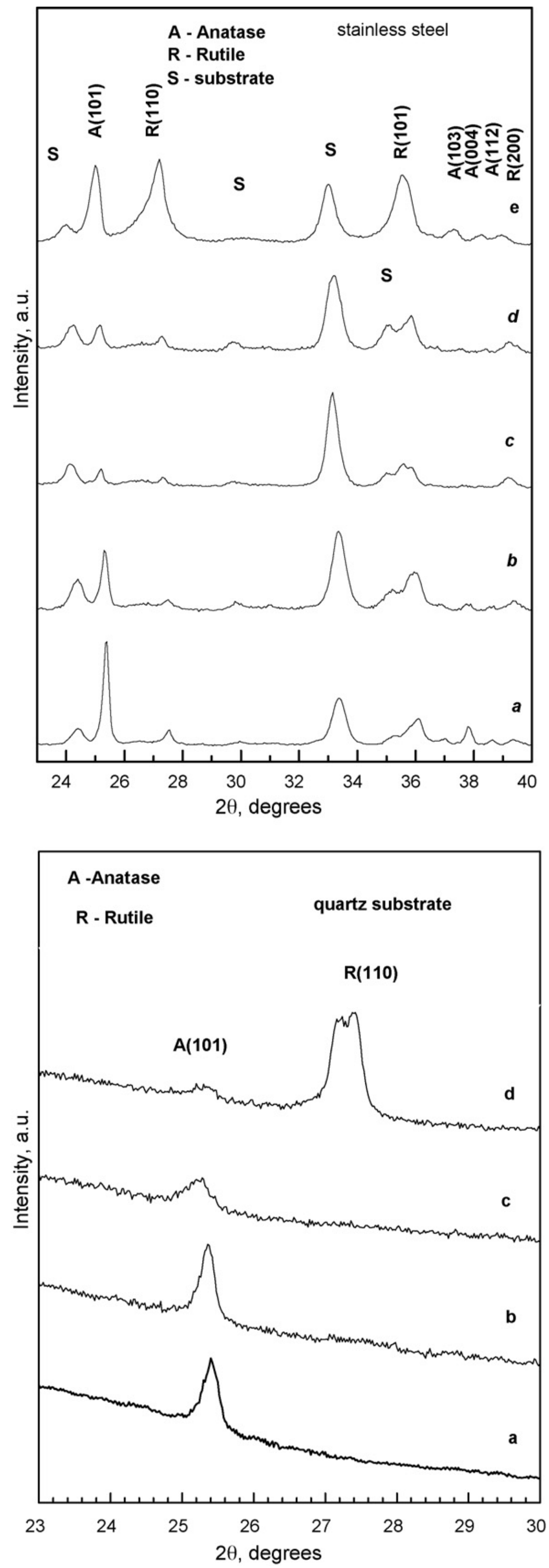

Fig. 4. XRD spectra of sprayed TiO_2 films doped with different SnO_2 content, annealed at 700 °C on stainless steel: (a) 0 mol%, (b) 3 mol%, (c) 10 mol%, (d) 20 mol% and (e) 50 mol% and on quartz substrate (a) 0 mol%, (b) 3 mol%, (c) 20 mol% and (d) 50 mol%.

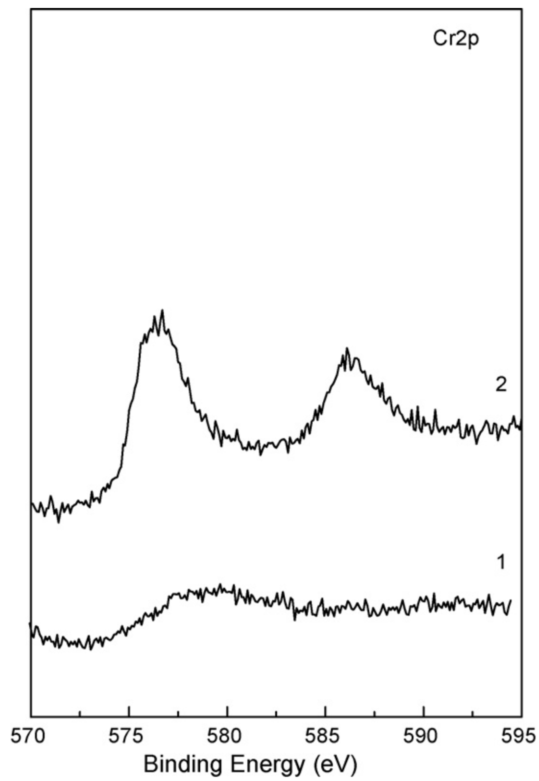

Fig. 5. XPS spectra of Cr2p of TiO_2 films on stainless steel: (1) TiO_2 treated at 500 °C and (2) TiO_2–3 mol% SnO_2, treated at 700 °C.

well as Fe and Cr, penetrated in the TiO_2 films from the steel substrate.

Fig. 6 shows the XPS spectra of Ti2p and Sn3d of TiO_2–SnO_2 (20 mol%) films on stainless steel, annealed at 500 °C. The concentration of oxygen, titanium and tin in the films after spraying and thermal treatment are 65; 9.7 and 19.9 at.%, respectively. It can be seen that the dopant concentration on the films surface is several times higher than that inside the film. This fact can be explained by the precipitation of dopant. Similar behaviour of the dopant was previously established by us in the sprayed SnO_2 and ZnO films [25,26].

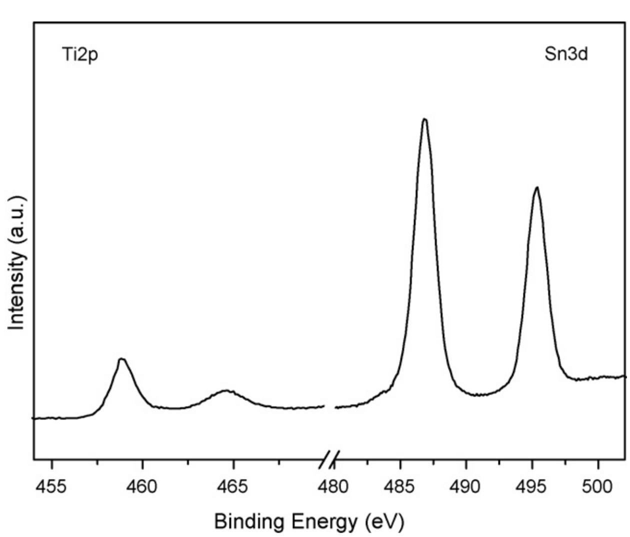

Fig. 6. XPS spectra of Ti2p and Sn3d of TiO_2–20 mol% SnO_2 films on stainless steel, treated at 500 °C.

The grain size of crystallites in the films doped with a certain amount of SnO_2 on stainless steel changes slightly after the treatment at different temperatures (500–800 °C, Table 1). As seen from the table, the sizes of the crystallites of TiO_2–SnO_2 films on stainless steel are smaller than the corresponding ones deposited on quartz substrate. This result could be explained by the difference of thermal conductivity of the substrates. When the solution droplets reach the substrate surface, the droplets consume thermal energy for their reactive condensation and solvent evaporation. The stainless steel has a higher thermal conductance than the quartz and, therefore, the substrate temperature of stainless steel remains higher during the spraying than that of the quartz substrate. The droplet evaporation rate on the steel is higher and hence the degree of supersaturation increases, which may lead to the formation of a large number of nanometer size crystallites [31].

4. Conclusions

Thin nanosized TiO_2–SnO_2 films, deposited on quartz and stainless steel substrates, are obtained by spray pyrolysis method. In both cases the crystalline phase transformation from anatase to rutile is promoted by the increase of SnO_2 content in the TiO_2 films and the heat-treatment temperature. It is found that the type of substrate has a significant effect on the phase composition and the anatase phase stability. The sprayed films deposited on quartz consist of pure anatase up to 700 °C, while the films on stainless steel contain a mixture of anatase as the main phase and some rutile crystallites. These phenomena are probably caused by the interactions between substrate and film. Silica stabilizes the anatase in the case of TiO_2 films deposited on quartz substrates.

The combined effect of SnO_2 doping and the penetration of iron and chromium from the steel for sprayed TiO_2–SnO_2 films probably causes a pronounced crystallization of rutile. The TiO_2–SnO_2 films deposited on quartz possess crystallites sizes in the range 25–45 nm, while on stainless steel they are about 23 nm.

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