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Effect of substrate type, dopant and thermal treatment on physicochemical properties of TiO_2–SnO_2 sol–gel films

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Abstract. **Thin nanocrystalline TiO_2–SnO_2 films (0–50 mol% SnO_2) were prepared on quartz and stainless steel substrates by sol–gel coating method. The obtained films were investigated by XRD, Raman spectroscopy and XPS. The size of the nanocrystallites was determined by XRD–LB measurements. We ascertained that the increase of treatment temperature and concentration of SnO_2 in the films favour the crystallization of rutile phase. The substrate type influences more substantially the phase composition of the TiO_2–SnO_2 films. It was established that a penetration of elements took place from the substrate into the films. TiO_2 films deposited on quartz substrate include a Si which stabilizes anatase phase up to 600 °C. The films which are deposited on stainless steel substrate and treated at 700 °C show the presence of significant quantity of rutile phase. This phenomenon could be explained by the combined effect of Sn dopant as well as Fe and Cr, which also are penetrated in the films from the steel substrate. The titania films doped up to 10 mol% SnO_2 on stainless steel possess only 12–17 nm anatase crystallites, whereas the TiO_2–(10–50 mol%) SnO_2 films contain very fine grain rutile phase (4 nm).**

Keywords. **TiO_2–SnO_2 films; sol–gel; anatase; rutile; quartz substrate; stainless steel substrate.**

1. Introduction

Titania (TiO_2) has recently attracted much attention because of its large surface area and pores, which are of great importance in self-cleaning glasses, gas sensors, optical thin-layer instruments, antireflection coatings for photovoltaic cells, photo chromic devices (Hoffman *et al* 1995; Traversa *et al* 1996; Garzella *et al* 2000; Miyauchi *et al* 2002; Habibi *et al* 2007; Shen *et al* 2009) etc. The choice of the dopant in titania may play a crucial role in the crystalline structure and phase transformation temperature of TiO_2 thin films. The TiO_2–SnO_2 system is attractive due to the close ionic radii, equivalency, thermal stability and advantages for environmental improvements. A coupled TiO_2–SnO_2 photocatalyst has been reported to work efficiently for degradation of various organic pollutants under UV-VIS irradiation (Kanai *et al* 2004; Maeda and Hirota 2006; Zhou *et al* 2008; Tu *et al* 2009; El-Maghraby 2010). It is known that the SnO_2 influences some physicochemical properties of TiO_2, especially when the addition of SnO_2 to titania films reduces the size of the crystallites and inhibits their growth (Lin *et al* 1999; Zakrzewska 2001; Liu *et al* 2002). The literature review about crystalline stability of TiO_2–SnO_2 system is still confused. It was indicated that tin oxide in TiO_2–SnO_2 binary oxides stabilizes the anatase phase up to 700 °C (Liu *et al* 2002; Yang *et al* 2002), however, other reports revealed that the addition of SnO_2 serves as a nuclei for the phase transformation and reduce the anatase–rutile transition temperature (Tai and Oh 2002; Mahanty *et al* 2004; Kumar *et al* 2007). There is a lack of systematic studies concerning the effect of the type of used substrate on the phase composition and crystallite size of TiO_2 and TiO_2–SnO_2 films, especially in the cases when the films are deposited on steel substrates. This investigation is of great importance concerning the possible applications of them as photocatalytic electrodes (Kaya *et al* 2005) and anticorrosion coatings (Fallet *et al* 2001). Fernandez *et al* (1995) have proved migration of some cations from the support to the TiO_2 layers: Na^+ and Si^{4+} from glass and Fe^{3+} and Cr^{3+} from stainless steel, which has detrimental effect on the photocatalytic activity of the films. In our previous report about TiO_2–SnO_2 sprayed films on quartz and stainless steel, we have found that the type of substrate and SnO_2 content in the films has a significant effect on the phase composition and anatase phase stability (Stambolova *et al* 2010).

The aim of this paper is to investigate the influence of thermal treatment temperature, type of the substrate and concentration of tin dioxide in TiO_2 films on anatase-phase stability and size of the crystallites of titania sol–gel films.

2. Experimental

Titanium precursor solution was prepared by mixing 0·35 M $Ti(i\text{-}OPr)_4$ with acetylacetone and dissolving in isopropanol–water mixture. The resultant solution had molar ratio

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between Ti(*i*-OPr)$_4$:*AcAc*:H_2O:*iso*PrOH = 1:1:1:30. Then the titania sol was mixed with 0·2 M $SnCl_4$ in ethanolic solution in order to obtain final sols with 0–50 mol% tin dioxide. To prevent the hydrolysis of $SnCl_4$ solution, a few drops of HNO_3 were added to the reaction mixture. Finally 10 wt% polyethyleneglycol (PEG) with a molecular weight of 400 was added to the mixture of Ti(OPr)$_4$ and $SnCl_4$ under vigorous stirring and the final polymeric solution was continuously stirred for 1 h. Quartz and stainless steel were used in order to investigate the effect of substrate type. The quartz substrates were cleaned successively with dichromate mixture, mixture of hydrochloric acid and nitric acid (3:1), ethanol and acetone. The stainless steel plates were cleaned successively in hot ethanol and acetone. The substrate were coated with sol solution by spin-on technique, and then dried after every deposition at 60, 100 and 300 °C for 10 min. The drying procedure was repeated four times. The final thermal treatment (after froth drying) was carried out in air at 500–800 °C for 60 min and thick films (∼150 nm) were obtained. The crystalline phase composition of the samples was studied by X-ray diffraction (XRD) using X-ray diffractometer (Philips PW 1050) with CuK_α radiation. XRD–LB measurements were carried out in order to estimate the crystallite size. Raman spectra were recorded using a SPEX 1403 double spectrometer, equipped with a photomultiplier, working in photon counting mode. The 488 nm line of an Ar^+ ion laser was used for excitation. The chemical 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 AlK_α radiation with an energy of 1486·6.eV.

3. Results and discussion

3.1 *Films deposited on quartz substrate*

Figure 1 presents the Raman spectra of the sol–gel TiO_2 doped with 1–15 mol% SnO_2 films on quartz substrates and annealed at 500 °C. Raman peaks at 144, 197, 396, 516 and 638 cm^{-1} are assigned to the anatase phase (Buska *et al* 1994). The Raman spectra for the TiO_2 films doped with 20 and 50 mol % SnO_2 have only peaks assigned to the substrate used. XRD profiles of these films indicate the presence of anatase phase. The anatase crystallites remain after annealing at 600 °C. Rutile becomes the main crystalline phase for all films investigated after heat treatment at 700 °C. XPS analysis revealed that the films include silicon content and is in the range 2·5–3·5 at%. This might be explained by interaction of quartz substrate with films. We have observed similar process for sprayed ZrO_2 films, which are deposited on quartz substrate (Peshev *et al* 2003). The possible mechanism used in the interaction is not yet clear. Probably SiO_2 inclusion in sol–gel films might stabilize the anatase phase. This hypothesis is in accordance with the results obtained by Yoshinaka *et al* (1997), where it is proved that the addition of 5 mol% SiO_2 to TiO_2 has some retarding effect on the anatase to

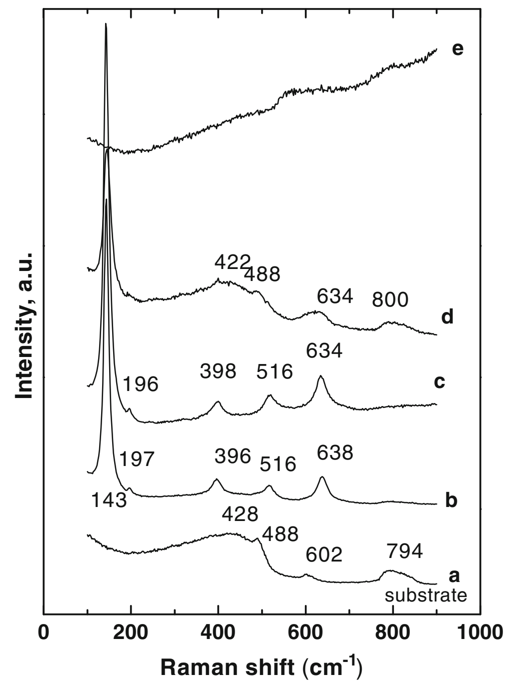

Figure 1. Raman spectra of sol–gel TiO_2 films doped with different SnO_2 contents, annealed at 500 °C on quartz substrates: (a) substrate, (b) 1 mol%, (c) 5 mol%, (d) 10 mol% and (e) 50 mol%.

rutile transformation. In conformation, Nikolic *et al* (2005) have found that the transformation rate of TiO_2 sol–gel films is lower on quartz and single crystal quartz than on alumina substrate.

3.2 *Films deposited on stainless steel substrate*

XRD profiles of pure titania films and films doped with 3 and 5 mol % SnO_2 (treated at 500 °C) indicate that only the peaks are assigned to anatase crystallites (figures 2a–c). Rutile peaks are observed for the sample doped with 10 mol% SnO_2 (figure 2d). With the increase of tin dioxide content in the films, peaks assigned to anatase fade out and the rutile peaks appear. Undoped titania films annealed at 700 °C show mainly anatase phase with traces of rutile, (figure 3). All sol–gel films doped with SnO_2 (10–50 mol %) and treated at 600–700 °C contain mainly rutile phase. The cassiterite phase has not been registered by XRD analysis probably due to the fact that SnO_2 peak overlaps with the strongest rutile one or it is in the amorphous state. Figure 4 shows X-ray diffractogram of TiO_2 doped with 10 mol% SnO_2 after treatment at 700 °C. It is known that the rutile phase is the most stable when the grain size is >35 nm (Zhang and Banfield 2000). In the TiO_2–SnO_2 films deposited on steel substrates, a lower anatase–rutile transformation is observed despite smaller crystallites of size less than 35 nm. Subsequently, the introduction of SnO_2 to our titania films probably has more pronounced effect on the transformation to rutile than size of the crystallites. The possible explanation is that the cassiterite has a rutile structure and thus promotes phase transition (Ding *et al* 1994; Mahanty *et al* 2004).

The chemical composition of sol–gel TiO_2–SnO_2 (0–50 mol%) films was investigated by XPS. XPS analysis indicated some interaction between stainless steel substrate and films likely in the case of films deposited on quartz substrate. It was established that 4 at% iron from stainless steel substrate penetrates into the films and the concentration is not changed with treatment at temperatures up to 700 °C. Gennari and Pasquevich (1998) revealed that the dopant Fe_2O_3 decreases the phase transition temperature of TiO_2 powdery samples. The strong promoting effect of iron addition to titania on the anatase–rutile transition has been established also by other workers (MacKenzie 1975; Zhang and Reller 2002).

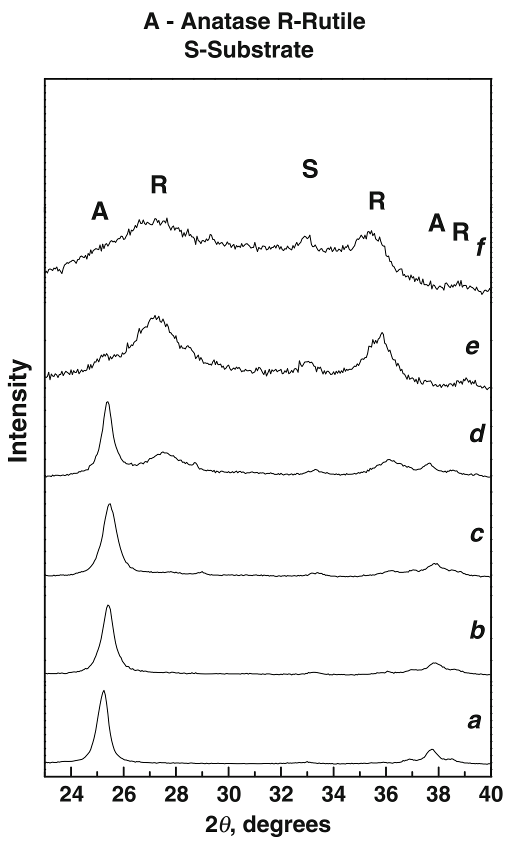

Figure 2. XRD spectra of sol–gel TiO_2 films doped with different SnO_2 contents, annealed at 500 °C on stainless steel: (a) 0 mol%, (b) 3 mol%, (c) 5 mol%, (d) 10 mol%, (e) 20 mol% and (f) 50 mol%.

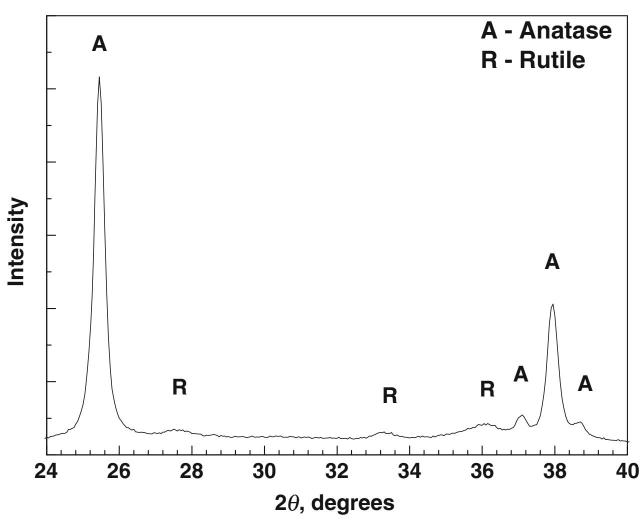

Figure 3. XRD spectra of sol–gel TiO_2 films, annealed at 700 °C on stainless steel.

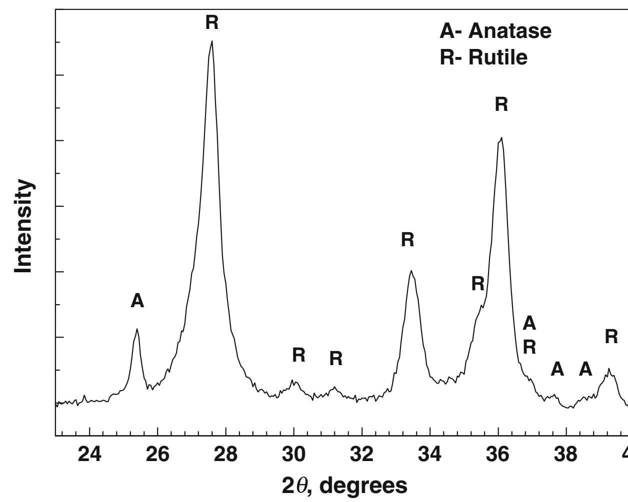

Figure 4. XRD spectra of sol–gel TiO_2 films doped with 10 mol% SnO_2, annealed at 700 °C on stainless steel.

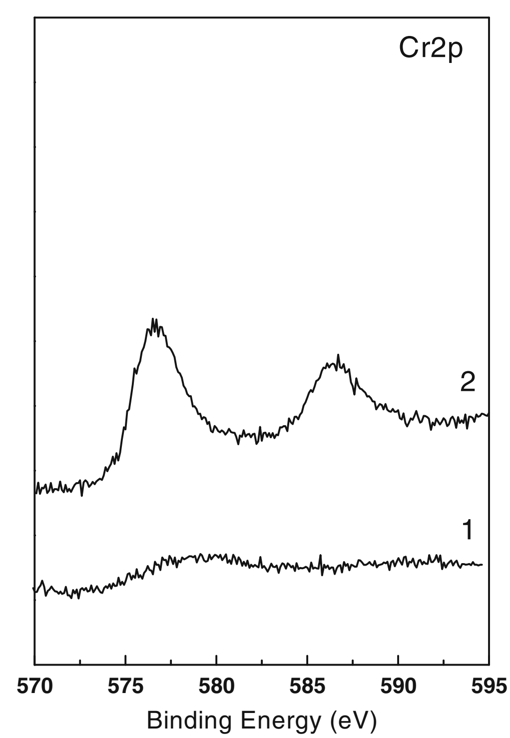

Figure 5. XPS spectra of Cr2*p* of TiO_2 sol–gel films on stainless steel: (1) TiO_2 treated at 500 °C and (2) TiO_2–10 mol% SnO_2, treated at 700 °C.

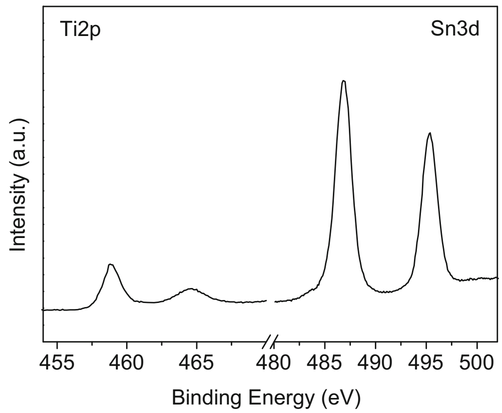

Figure 6. XPS spectra of Ti2*p* and Sn3*d* of TiO_2–20 mol% SnO_2 sol–gel films on stainless steel treated at 500 °C.

Table 1. Size of anatase crystallites in TiO_2–SnO_2 sol–gel films after thermal treatment at 500 °C.

Sample (mol% SnO_2)	Crystalline size for films deposited on quartz substrate (nm)	Crystalline size for films deposited on stainless steel substrate (nm)
0	16	16
1	16	15
3	15	15
5	14	12·5
10	14	17 (4·5 for rutile phase)
20	14	– (4 for rutile phase)
50	14·5	– (5 for rutile phase)

It was established that chromium penetrates from the steel substrate into the films treated at 500 °C. The X-ray photoelectron spectrum of the Cr 2*p* region for titania films, treated at 500 and 700 °C is shown in figure 5. The concentration of Cr in the films was about 2 at% at 500 °C. The thermal treatment at 700 °C caused more pronounced diffusion of chromium ion from the steel substrate and its concentration in the films increases up to 6·7 at%. The addition of 1 mol% Cr into titania powder leads to 9% rutile phase according to the investigation of MacKenzie (1975). A partial rutilization of TiO_2 supported catalyst during thermal treatment has also been reported (Fernandez *et al* 1995). In the doped TiO_2 films, treated at 700 °C, presence of significant quantity of rutile phase could be explained by the combined effect of Sn dopant as well as Fe and Cr ions, which are penetrated in the TiO_2 films from the steel substrate. It was proved by XPS analyses that the dopant concentration in the basic layer is slightly lower than that in the sol solution. Figure 6 presents XPS spectra of Ti2*p* and Sn3*d* of TiO_2–20 mol% SnO_2 sol–gel films on stainless steel, annealed at 500 °C. The concentration of oxygen, titanium and tin in the TiO_2 films after sol–gel procedures and treatment are 69·8, 12 and 11·6 at%, respectively. We have evaluated the crystallites size of the films on the basis of well known Scherrer's equation. In our opinion these values are more representative than the microscopic photographs. By TEM or AFM method, we can gather information about the grains size, which consisted of crystallites. The data in table 1 reveal that the addition of SnO_2 (10–50 mol%) reduces slightly the grain dimensions due to the grain growth inhibition. A similar phenomenon was also observed by other workers (Zakrzewska 2001). The dimensions of the rutile crystallites were found to be very small (4–4·5 nm), while the anatase crystallites have a size 12·5–17 nm.

4. Conclusions

In this report we proved that 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 was also found that the type of substrate has a significant influence on the phase composition and anatase phase stability. Anatase crystallites in the sol–gel TiO_2–SnO_2 films deposited on quartz substrates were found to be more stable as compared to the stainless steel substrate. This phenomenon might come from the impurity effects of SiO_2 provided by the quartz substrate. In the case of sol–gel films deposited on stainless steel, the rutile peaks appeared at 500 °C. For the films treated at 700 °C, the presence of significant quantity of rutile phase might be explained by the combined effect of Sn dopant as well as Fe and Cr, which penetrated into the TiO_2 films from steel substrate. It is interesting to highlight that those very small dimensions of rutile crystallites (4 nm) have been obtained for TiO_2 films doped with 10–50 mol% SnO_2.

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