

# Synthesis of thin dense titania films via an aqueous solution-gel method

I. Truijen · M. K. Van Bael · H. Van den Rul ·  
J. D'Haen · J. Mullens

Received: 4 January 2006 / Accepted: 19 May 2006 / Published online: 10 October 2006  
© Springer Science + Business Media, LLC 2006

**Abstract** Nanostructured titanium dioxide films have been reported to be used in many applications ranging from optics and solar energy devices to gas sensors. This work describes the synthesis of nanocrystalline titania films via an aqueous solution-gel method. The thin films are deposited by spin coating an aqueous citratoperoxo-Ti(IV)-precursor solution onto a silicon substrate. The influence of processing parameters like  $Ti^{4+}$  concentration and crystallization temperature on the phase formation, crystallite size and surface morphology of the films is studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM). Furthermore, the effect of successive layer deposition on the film thickness of the resulting films is studied by means of cross sectional SEM. SEM and TEM micrographs clearly show that, after optimization of the process parameters, thin, smooth, dense nanocrystalline films are synthesized in a reproducible manner. The films are composed of 15–20 nm

grains. At higher crystallization temperatures (600, 650°C) also larger particles (40–70 nm) are present. XRD data reveal that a phase pure anatase film is formed at 450°C. Crystallization temperatures equal to or higher than 600 °C however give rise to the formation of both the anatase and rutile crystalline phases. The smoothness of the films is proved by their very low rms surface roughness ( $\leq 1.1$  nm) measured by AFM.

**Keywords** Anatase · Rutile · Water based · Chemical solution deposition

## 1 Introduction

Recently, nanocrystalline titanium dioxide films are being studied intensively because of their potential utilization as a material in photocatalysis [1–4], photovoltaics [5,6] or gas sensors [7]. Compared to other semiconductors titanium dioxide is favoured for these applications, due to the fact that it has a high photoactivity, it is biologically and chemically inert, readily available and cheap. The production of  $TiO_2$  films has been carried out by several methods, such as sputter techniques [8], chemical vapour deposition (CVD) [9] and the sol-gel method [10–12]. The sol-gel route allows for the simple production of large area, high purity films. Moreover, this process allows a precise control of film thickness, particle size and porosity by adjusting different parameters such as metal ion concentration, calcination temperature, etc.

The sol-gel route usually starts from metal oxides, salts or alkoxides, dissolved in alcoholic solvents, implying a relatively high cost and ecological risk [10]. This work describes the synthesis of nanocrystalline thin dense titania layers via an aqueous solution-gel method. The aqueous route shows the same advantages as its conventional alcoholic counterpart

---

I. Truijen · M. K. Van Bael · H. Van den Rul · J. D'Haen ·  
J. Mullens (✉)  
Hasselt University, Institute for Materials Research,  
Agoralaan–building D, B-3590 Diepenbeek, Belgium  
e-mail: jules.mullens@uhasselt.be

I. Truijen  
e-mail: ine.truijen@uhasselt.be

M. K. Van Bael  
e-mail: marlies.vanbael@uhasselt.be

H. Van den Rul  
e-mail: heidi.vandenrul@uhasselt.be

J. D'Haen  
e-mail: jan.dhaen@uhasselt.be

M. K. Van Bael · H. Van den Rul · J. D'Haen  
IMEC vzw, Division IMOMECE,  
Agoralaan – building D, B-3590 Diepenbeek, Belgium

but it has the surplus of being economically and ecologically friendly, regarding the precursor synthesis. Furthermore, no special precautions to protect the starting products from air or humidity have to be taken. However, the use of water as a solvent is not very obvious. High valence metal ions like  $Ti^{4+}$  are very reactive in water and hydrolyse very easily. Therefore, the reactive tetravalent Ti ion is encapsulated in a citratoperoxo-Ti(IV) complex [13, 14]. In this complex Ti is surrounded by organic ligands with strong electron donating functionalities like carboxylate groups. In this way hydrolysis and subsequent uncontrolled precipitation of hydroxides and oxides are prevented. Upon evaporation of the water an amorphous gel is formed, which is thermally treated in order to obtain nanocrystalline titania.

In our study a simple technique, namely spin coating, is used in order to deposit the aqueous Ti(IV)-precursor solution. To our knowledge, the preparation of thin dense titania films via an aqueous solution-gel method has not been investigated so far.

## 2 Experimental

### 2.1 Materials and reagents

Starting materials for the preparation of the citratoperoxo-Ti(IV)-precursor solution are Ti(IV)-isopropoxide ( $Ti(iOPr)_4$ , 98 + %, Acros), citric acid ( $C_6H_8O_7$ , 99%, Aldrich), hydrogen peroxide ( $H_2O_2$ , 35 wt.% in  $H_2O$ , p.a., stabilized, Acros) and ammonia ( $NH_3$ , 32% in  $H_2O$ , extra pure, Merck).

### 2.2 Precursor synthesis

The procedure to prepare the citratoperoxo-Ti(IV)-precursor solutions, with  $Ti^{4+}$  concentrations starting from 0.2 M up to 1.0 M, is reported in previous work [13–16]. First, Ti(IV)-isopropoxide is hydrolysed in  $H_2O$ , which leads to the precipitation of a hydroxide. In a next step, citric acid and  $H_2O_2$  are added to this precipitate in a 2:1 and 1.2:1 molar ratio against  $Ti^{4+}$ , respectively. The pH of the resulting citratoperoxo-Ti(IV) solution is adjusted to pH = 7 using ammonia. A clear, yellow, stable solution is obtained.

### 2.3 Preparation of thin $TiO_2$ films

In order to improve the wettability of the substrate for the aqueous precursor solution, prior to deposition, the hydrophilicity of the substrates is optimized by chemical treatment of its surface using a two step SPM/APM (sulphuric acid peroxide mixture/ammonia peroxide mixture) cleaning method [17]. In our experiment titania layers are prepared on silicon wafer substrates ( $SiO_2/Si$ , 2.5 cm  $\times$  2.5 cm). Rotation

speed and time are set on 3000 rpm and 30 s respectively. Each deposited layer is subjected to a thermal treatment consisting of three steps: a drying step at 180 °C, a pyrolysis step at 300 °C and a second pyrolysis step at  $T_{\text{cryst}}$  °C. All three steps are carried out on a hot plate in ambient air. For a final crystallization step, after deposition of the last layer, the samples are placed in a horizontal tube oven and heated in dry air at a heating rate of 10 °C/min from room temperature to 450, 500, 550, 600 and 650 °C, followed by an isothermal step at this temperature for 60 min.

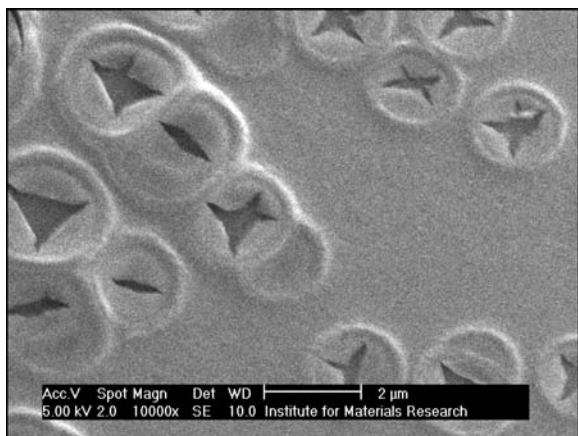
### 2.4 Characterization techniques

The metal ion concentration in the precursor solution is determined by means of inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a Perkin-Elmer Optima 3000DV. Thermal analysis experiments on the precursor gel are performed using thermogravimetric analysis (TGA) carried out on a TA Instruments TGA 951–2000. The gel powder is obtained by drying the 0.4 M citratoperoxo-Ti(IV)-precursor solution in a Petri dish at 60 °C for 18 h. The TGA and DTG data are measured at a heating rate of 5 °C/min in an atmosphere of 100 ml/min synthetic dry air (mixture of 20%  $O_2$  and 80%  $N_2$ ). Phase formation in the resulting films is studied at room temperature by X-ray diffraction (XRD) using a Siemens D-5000 diffractometer with  $Cu-K_{\alpha 1}$  radiation. Scanning electron micrographs (SEM) of the thin films are obtained on a Philips XL30-FEG SEM and on a FEI Quanta 200FEG-SEM, both equipped with secondary electron (SE) and back scattered electron (BSE) detectors. After removal of the underlying silicon substrate by etching with a 40 vol.% aqueous HF solution, transmission electron microscopy (TEM) is performed on the films using a Philips CM12-STEM. RMS surface roughness is measured by atomic force microscopy (AFM) using an Autoprobe CP from Park Scientific Instruments under ambient atmosphere. The measurements are performed in a non-contact mode using an etched silicon tip (Ultrasharp MikroMash NSC11 B). Film thicknesses are determined by means of cross sectional SEM.

## 3 Results and discussion

### 3.1 Optimal precursor concentration

In a first experiment different precursor concentrations, starting from 0.2 M up to 1.0 M  $Ti^{4+}$ , are used in order to determine an optimal  $Ti^{4+}$  concentration for the deposition of thin smooth layers. The experiment reveals that metal ion concentrations  $\geq 0.6$  M give rise to the formation of blistered films (Fig. 1). This can be explained by the fact that inherent to the increase of the metal ion concentration, also the

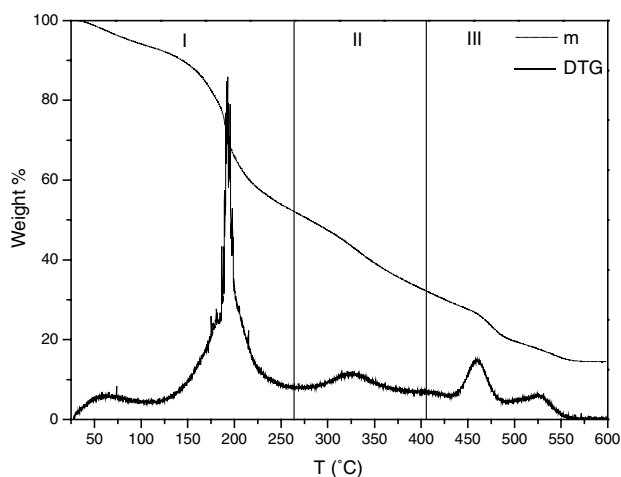


**Fig. 1** SE scanning electron micrograph of a blistered TiO<sub>2</sub> film

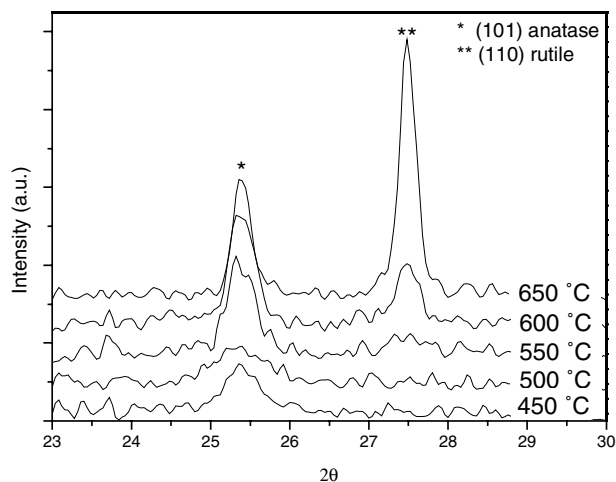
concentration of organic compounds increases. In this way larger amounts of gas have to be removed during thermal treatment, causing the formation of blisters. A 0.4 M Ti<sup>4+</sup> precursor solution is therefore used for further experiments.

### 3.2 Optimization of the thermal treatment

Thermogravimetric analysis (TGA) of the precursor gel powder is performed in order to determine a good initial thermal treatment profile for the preparation of titania thin films deposited out of the same precursor solution. In the DTG curve (Fig. 2) three regions of decomposition can be distinguished localized at 190, 320 and 470–545°C. At 190°C only water and ammonia are removed from the gel [14]. In the other steps the organic content is burned out [14]. To promote the formation of a smooth and uniform thin film, the precursor needs to be gradually decomposed. Therefore the choice of the drying and the first pyrolysis temperatures (as shown in Fig. 1) is based on the first two decomposition steps. The last



**Fig. 2** TG/DTG analysis of a 0.4 M Ti<sup>4+</sup> precursor gel in dry air (5°C/min)



**Fig. 3** XRD spectra of TiO<sub>2</sub> films composed of 3 layers and crystallized at different temperatures ( $T_{\text{cryst.}} = 450\text{--}650^\circ\text{C}$ )

hot plate step is a second pyrolysis step in order to obtain a complete removal of the organic matrix. The temperature of the second pyrolysis step has to lie in the temperature region, where, according to the DTG curve, the last weight losses occur. For each sample the temperature of the second pyrolysis step is chosen to be equal to the final crystallization temperature ( $T_{\text{cryst.}}^\circ\text{C}$ ) for that sample. Further, after deposition of the last layer, the samples are subjected to a final crystallization step.

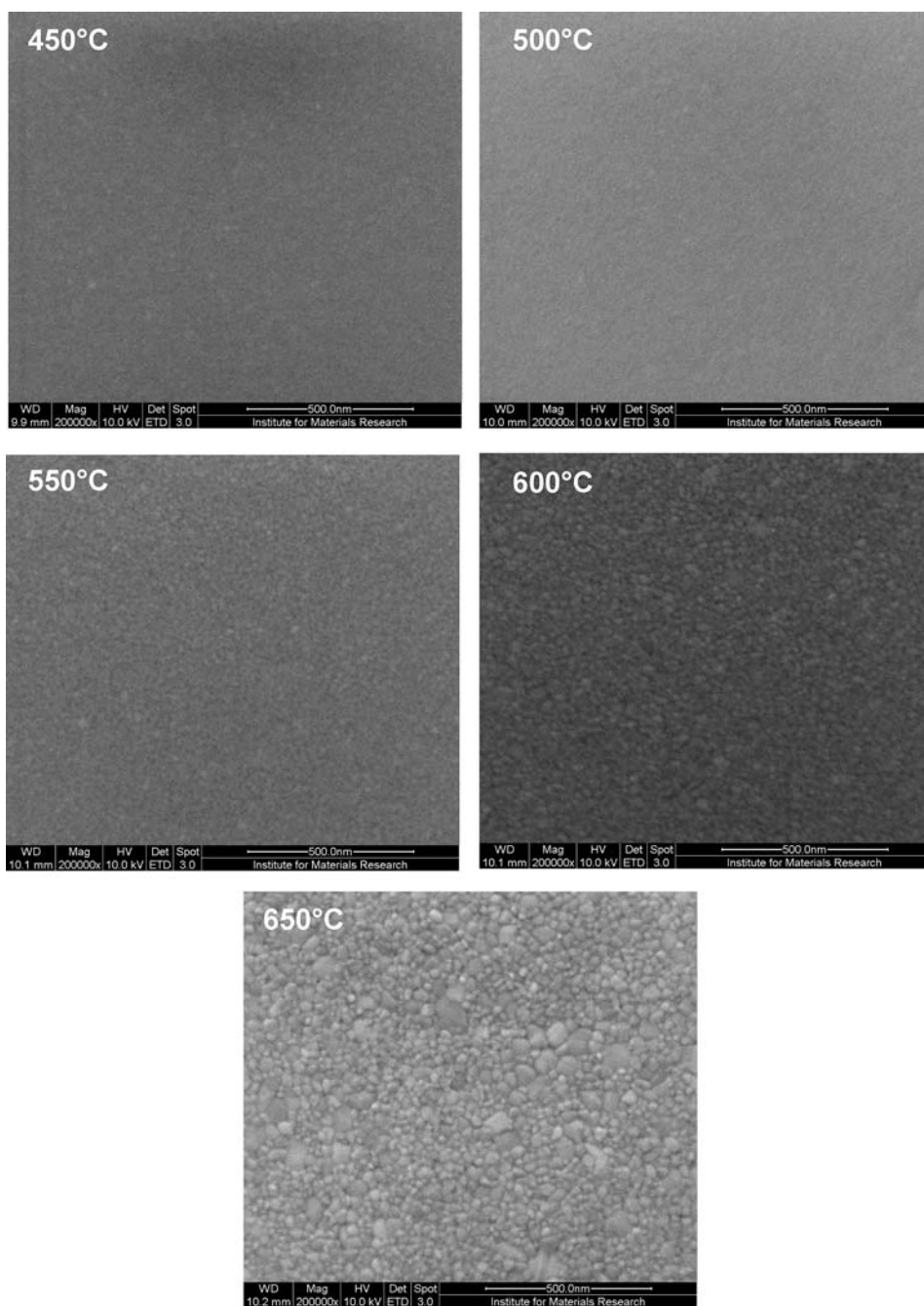
### 3.3 The effect of crystallization temperature on phase formation

In order to find an optimal crystallization temperature, the titania films are crystallized at different temperatures and studied by means of X-ray diffraction. XRD data (Fig. 3) indicate that a phase pure anatase film is formed using a crystallization temperature of 450°C. At crystallization temperatures  $\geq 600^\circ\text{C}$  both the metastable anatase and the stable rutile crystalline phases are present. The low intensity of the TiO<sub>2</sub> peaks can be attributed to the small thickness of the film.

### 3.4 The effect of crystallization temperature on morphology

The influence of the crystallization temperature on the morphology of the resulting films is also studied. SEM analysis shows (Fig. 4) more pronounced grain boundaries at higher crystallization temperatures. For the 550°C sample grains of 15 nm can be distinguished. Furthermore, this study reveals that the crystallization temperature also has an influence on the particle size. High crystallization temperatures (at 600°C and 650°C) lead to a small increase of the grain size of the primary particles (15–20 nm) and to the additional

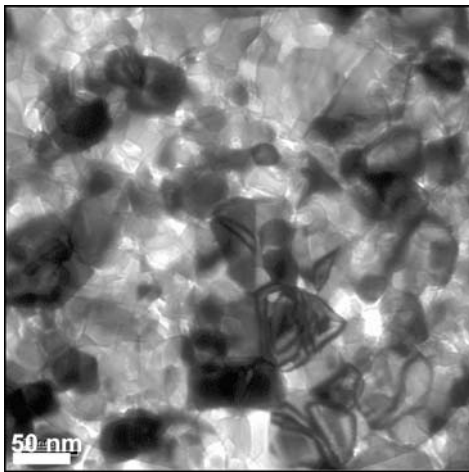
**Fig. 4** Plane view SE SEM images of titania films deposited on SiO<sub>2</sub>/Si crystallized at different temperatures



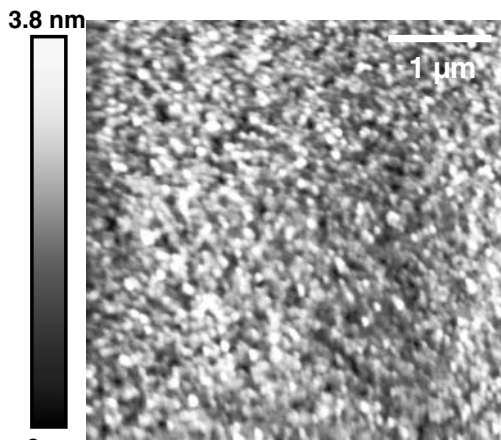
formation of larger grains (40–70 nm). These primary particles and larger grains can also be seen in a TEM image of the 650°C sample (Fig. 5). SEM and TEM analysis of the 600 and 650°C samples also shows that the resulting titania films have a dense character with a smooth surface. The smooth character of the resulting films is further proved by Atomic Force Microscopy (Fig. 6). An rms surface roughness of only 0.6 nm is obtained for a film composed of three layers. Even after deposition of ten layers, the rms roughness is still very low (1.1 nm). The silicon substrate shows an rms roughness of 0.3 nm.

### 3.5 Film thickness versus number of deposition steps

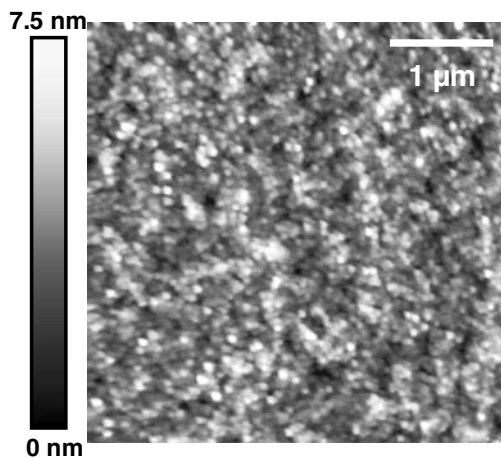
Spin coating experiments show that the film thickness of the resulting nanocrystalline titania films can be adjusted easily by the number of deposited layers. The effect of successive layer deposition on the film thickness of the resulting titania films is studied by means of cross sectional SEM analysis (Fig. 7) of films crystallized at 650 °C. As shown in Fig. 8 the film thickness increases linearly with the number of deposited layers. In this way a 180 nm thin film is obtained after 10 deposition cycles followed by a final crystallization step.



**Fig. 5** TEM image of a titania film composed of 3 layers and crystallized at 650°C

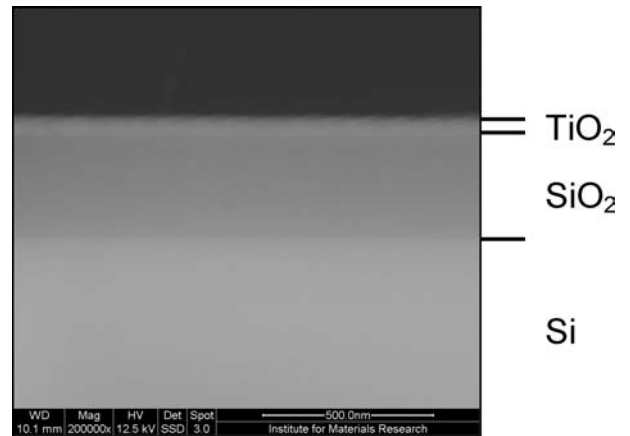


(a)

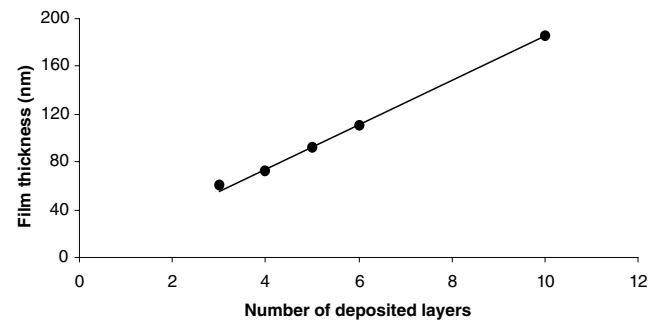


(b)

**Fig. 6** AFM topographic images (scan size 4 μm × 4 μm) of titania films crystallized at 650°C and composed of (a) 3 layers, (b) 10 layers



**Fig. 7** Cross sectional BSE scanning electron micrograph of a TiO<sub>2</sub> film composed of 3 layers



**Fig. 8** Film thickness vs. number of deposited layers determined by cross sectional SEM

#### 4 Conclusion

In this study it is shown that the presented aqueous solution-gel method enables the preparation of thin, smooth, dense, nanocrystalline TiO<sub>2</sub> films by spin coating the aqueous citratoperoxo-Ti-precursor solution onto silicon substrates. SEM and TEM micrographs clearly show that, after optimization of process parameters such as Ti<sup>4+</sup> concentration (0.4 M), crystallization temperature (650°C) and number of deposition cycles (10), a 180 nm thin, dense, nanocrystalline film is synthesized in a reproducible manner. The film is composed of 15–20 nm grains, with the presence of some larger particles (40–70 nm). XRD data reveal that the 650°C film is composed of both the anatase and rutile crystalline phase.

The nanostructured TiO<sub>2</sub> film prepared by the present method can be applied in photovoltaics, catalysis or gas sensing. Further investigations concerning the use of the film in photovoltaics are now in progress.

**Acknowledgements** M. K. Van Bael is a post-doctoral fellow of the Fund for Scientific Research Flanders, Belgium (FWO Vlaanderen). The authors would like to thank Dr. G. Vanhoyland, Dr. O. Douheret and Dra. I. Haeldermans of the Institute for Materials Research (Hasselt University) for performing the XRD, AFM and TEM measurements.

## References

1. Fujishima A, Rao TN, Tryk DA (2000) *J Photochem Photobiol C: Photochem Rev* 1:1
2. Kemmit T, Al-Salim NI, Waterland M, Kennedy VJ, Markwitz A (2004) *Curr Appl Phys* 4:189
3. Zhao L, Yu Y, Song L, Hu X, Larbot A (2005) *Appl Surf Sci* 239:285
4. Mellot NP, Durucan C, Pantano CG, Guglielmi M (in press) *Thin Solid Films*, corrected proof
5. Grätzel M (2001) *J Sol-Gel Sci Techno* 22(1–2):7
6. Grätzel M (2004) *J Photochem Photobiol A: Chem* 164:3
7. Skubal LR, Meshkov NK, Vogt MC (2002) *J Photochem Photobiol A: Chem* 148:103
8. Yamagishi M, Kuriki S, Song PK, Shigesato Y (2003) *Thin Solid Films* 442:227
9. Kang M, Lee JH, Lee SH, Chung CH, Yoon KJ, Ogino K, Miyato S, Choung SJ (2003) *J Mol Catal A: Chem* 193:273–283
10. Zhao G, Tian Q, Liu Q, Han G (2005) *Surf Coat Tech* 198:55
11. Hirashima H, Imai H, Miah MY, Bountseva IM, Beckman IN, Balek V (2004) *J Non-Cryst Solids* 350:266
12. Kitazawa N, Sakaguchi K, Aono M, Watanabe Y (2003) *J Mater Sci* 38, (14):3069
13. Van Werde K, Vanhoyland G, Nelis D, Mondelaers D, Van Bael MK, Mullens J, Van Poucke LC (2001) *J Mater Chem* 11(4): 1192
14. Hardy A, Van Werde K, Vanhoyland G, Van Bael MK, Mullens J, Van Poucke LC (2003) *Thermochim Acta* 397:143
15. Hardy A, Mondelaers D, Vanhoyland G, Van Bael MK, Mullens J, Van Poucke LC (2003) *J Sol-Gel Sci Techno* 26:1103
16. Hardy A, Mondelaers D, Van Bael MK, Mullens J, Van Poucke LC, Vanhoyland G, D'Haen J (2004) *J Euro Ceram Soc* 24: 905
17. Van Bael MK, Nelis D, Hardy A, Mondelaers D, Van Werde K, D'Haen J, Vanhoyland G, Van Den Rul H, Mullens J, Van Poucke LC, Frederix F, Wouters DJ (2002) *Integr Ferroelectr* 45:113