PREPARATION AND CHARACTERIZATION OF TiO_2-MnO SOL-GEL LAYERS ON GLASS

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Mixed oxide layer (TiO_2-MnO) was prepared by the sol-gel method using tetra-n-butyl-orthotitanate and manganese nitrate as precursors. Thermal transformation behaviour of the fresh xerogel was observed by thermal analysis. Sol-gel coatings were deposited by dip-coating method and the preparation of the films was finished by heat treatment. The surface of the layers was observed using optical microscope and by SEM. Good and uniform coatings were obtained from the peptised solutions. The film thickness was 147 and 158 nm for the second and third coating. After heat treatment, anatase and/or rutile crystals were observed in the layers according to the temperature of heat treatment which varied from 550°C to 800°C. Typical optical absorption peak of the films was observed using UV spectrophotometer in the range of 250-390 nm. The layers do not show any protection effect against water corrosion. The refractive index of the layers was found to depend on the number of subsequent coatings used for their preparation.

INTRODUCTION

Among various oxide layers, sol-gel derived titania layers show good optical quality and properties and are applicable for optoelectronic and electro chromic and many others devices [1]. In the past few years a lot of research work has been carried out on obtaining and investigating mixed titanium oxides such as $Ti_xV_{1-x}O_2$ [2], Ti-W oxide [3], Ti-Ce oxide [4]. The aim of this work was to modify optical properties like refractive index, optical absorption, chemical resistivity and other properties of the layers. The prime objective of this study was to prepare uniform sol-gel TiO_2-MnO thin layers on glass starting from procedures described in the literature [5-8]. Another objective was to determine some basic properties characterising the TiO_2-MnO thin layers and allowing a comparison of their characteristics with the layers consisting of pure TiO_2 [9]. Some of the properties (optical, photocatalytical) are given by the microstructure of the layers and strongly depend on the type of the TiO_2 crystals. For this reason attention has been paid to the identification of the anatase and rutile phase.

EXPERIMENTAL

Tetra-n-butyl-orthotitanate was used as the precursor for the preparation of titanium sol while glacial acetic acid was introduced in the reaction mixture to stimulate and ensure an exothermic reaction. The TiO_2 layers were prepared using sol-gel method. Details of the procedure used were described previously [5]. A mixture of CH_3COOH, ethanol and acetyl acetone was added to tetra-n-butyl-orthotitanate and the solution was diluted by adding a mixture of ethanol and water under continuous magnetic agitation at room temperature. A transparent gel was obtained after addition of ethanol, demineralised water and acetyl acetone. The manganese was introduced as nitrate Mn $(NO_3)_2$ $4H_2O$. The gel obtained from initial solution was dried at 80°C in air and 4.34 mg sample was analysed by scanning DTA-TGA technique (Stanton-Redcroft TG-750) in air. Scanning rate was adjusted to10°C.min^{-1}. Crystalline oxide formation was observed by X-ray diffraction technique using a Seifert XRD-3000P instrument with Co-Kα (λ = 0.179026 nm), graphite monochromator and radiation (40kV/40mA) operating at low diffraction angle.

Uniform coatings of TiO_2 - 0.25 MnO on glass substrate were obtained by dipping and drawing the glass from the colloidal solution. Coatings were prepared on cleaned glass substrates using the withdrawal speed of 10 cm/min, subsequently dried at 80°C for 2 hours and the final heat treatment was performed at 550°C for 1 hour. In order to study an influence of temperature on the composition of layers, also high temperature treatment was used up to 800°C. Silica glass was used in those cases as the substrate. The optical absorption of layers was investigated by UV spectrophotometer

(Shimadzu UV-1201-make) in the spectral range of 200-800 nm. The refractive index as a function of wavelength was measured with the AvaSpec-2048 Fiber Optic Spectrometer. This is based on the AvaBench-75 symmetrical Czerny-Turner spectrometer yielding maximum wavelength resolution of 0.5 nm.

The observation of surface of the films was realized with help of the light microscope Nikon E400 POL and by the electron microscope Hitachi S-4700 with two magnifications 200 nm and 500 nm.

The protection effect of layers against corrosion of glass surface in water was followed by immersing the substrates with films into 25 ml of demineralised water in closed containers. The samples were corroded by water at 80°C for different time periods (10 minutes, 1, 2, 4, 8 hours and 1, 2, 4 days). After that AAS analysis was performed to measure the concentration of Na+ ions in the water. The same test was carried out for the substrate without any coating (blank) to compare the corrosion of substrate with and without any coating.

RESULTS AND DISCUSSION

The TiO_2-MnO xerogel was investigated by DTA and TG technique (figure 1). Exothermal part, localized between 200°C and 450°C, showed processes of oxidation of the organic residuals while exothermal peak at 550°C should be attributed to evaporation and combustion of organic residuals while exothermic peak at 550°C probably corresponds to the crystallization of TiO_2 in form of anatase. The hardly distinct peak at 650°C can be explained by transformation of anatase into rutile form. The origin of the small endothermic peak at 950°C is not clear but the process responsible for the peak does not have any influence on the film formation.

The figures 2a, 2b and 2c show the results of X-ray diffraction analysis for samples prepared at various temperatures and with different coatings number.

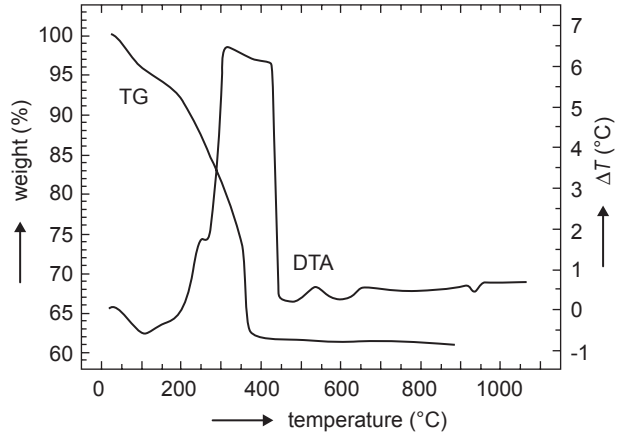
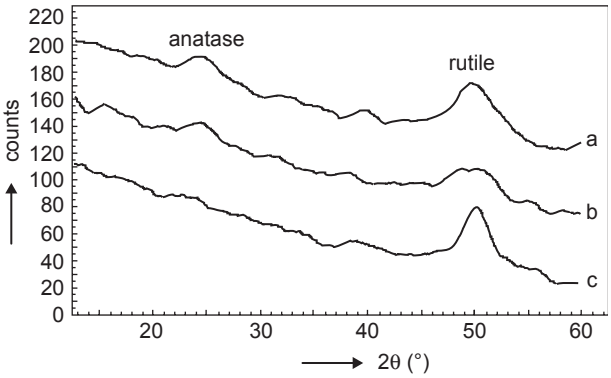
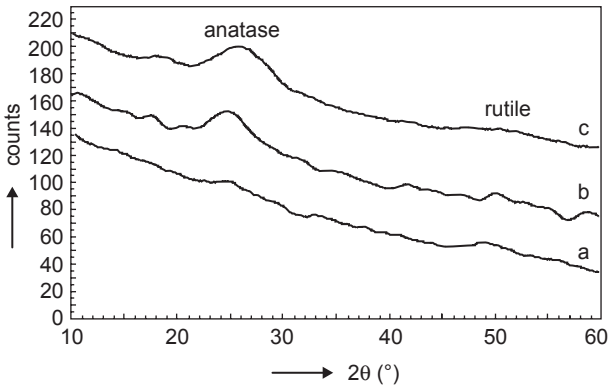


Figure 1. DTA and TGA thermograms of TiO_2-MnO xerogel.

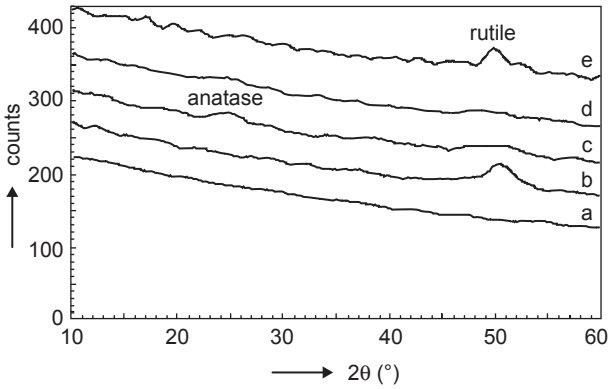
The XRD results are summarised in the table 1. It is clear that anatase was detected at 600°C while rutile was not found at all at this temperature. The effect corresponding to the anatase formation is more pronounced at layers created by subsequent coating of more films (see figure 2b). Both rutile and anatase were observed in layers consisting of two and three films at 700°C when



a - 1 hour, 700°C, 3 films layer; b - 1 hour, 700°C, 2 films layer; c - 1 hour, 750°C, 2 films layer



a - 1 hour, 600°C, 1film layer; b - 1 hour, 600°C, 2 films layer; c - 1 hour, 600°C, 3 films layer



a - substrate without any layer; b - 8 hours, 800°C, 1 film layer; c - 8 hours, 700°C, 1 film layer ; d - 8 hours, 600°C, 1 film layer; e - 1 hour, 800°C, 1 film layer

Figure 2. X-ray diffraction patterns of TiO_2-MnO layers.

calcinations period was one hour (figure 2a). Also 2 films layer tempered at 750°C for two hours consists of both crystalline forms with predominating rutile modification. In the layers prepared by one coating and tempered at 800°C only rutile was observed. The formation of anatase or rutile crystalline form is clearly affected by the number of films coated and the temperature of 800°C is necessary to get layers consisting purely of rutile form (see also table 1). From the XRD results follows that layers prepared at the lower temperatures consist of anatase, while rutile layers can be obtained only by higher temperatures, i.e. glasses with the softening point above 700°C have to be used as the substrate. The results presented here are in a good agreement with the literature, where the transformation of anatase into rutile is considered to proceed at temperatures above 700°C [10].

Figure 3 illustrates the UV - visible spectra of TiO_2-MnO layers measured in the wavelength range of 200-400 nm. Absorbance value was found to be increasing with increasing film numbers. TiO_2-MnO films show higher values of absorbance comparing to pure TiO_2 layers, but the peaks position and increased absorbance maximum and also their shift with the number of films to the higher wavelength values is very similar [5]. It is difficult to explain the absorbance curves and their change with the films number but increasing number of optical interfaces and resulting light interference might be probably responsible for this behaviour.

The figure 4 illustrates results of measurement of protection effect of layers against water corrosion. As it is seen, the TiO_2-MnO layer showed no significant protection effect against corrosion of the substrate. If we compare the protection against corrosion between TiO_2 and TiO_2-MnO layers, it is possible to conclude that TiO_2 and TiO_2-MnO films have similar small and negligible protection effect against corrosion [9].

Finally also the appearance and microstructure of the layers was investigated. No defects visible by eye were observed in the films. The layers were smooth, highly uniform and showed good adhesion onto the substrate. This characteristic of TiO_2-MnO is similar with the TiO_2 films but the crystals formed in presence of MnO showed a more rounded form.

Figures 5a and 5b show the thickness of TiO_2-MnO layers on glass measured by means of SEM micrographs. The average value of the layer thickness is about 150 nm for two and three films layer. The increase of thickness between the layers consisting of two and three films was surprisingly found to be almost negligible (about 10 nm). The TiO_2-MnO layers showed a smaller variation in the thickness when the number of films was increased in comparison to TiO_2 films. No reliable results of thickness measurement were obtained for the layer prepared by only one coating.

Figure 6 shows the values of refractive index in different wavelengths for TiO_2-MnO films with different coatings number. The refractive index values were decreased when the films number increased in the range of the wavelength up 400 nm. The one film layer have then nearly constant value of refractive index close to the value of 2.1, while the dependence for the two and three films layers shows continuous decrease with

Table 1. Influence of time, films number and temperature on the formation of rutile and anatase in the TiO_2-MnO layers.

Time	Films	Temperature	Rutile	Anatase
1 hour	1	600°C	(-)	(-)
1 hour	2	600°C	(-)	(+)
1 hour	3	600°C	(-)	(+)
8 hours	1	600°C	(-)	(-)
1 hour	2	700°C	(+)	(+)
1 hour	3	700°C	(+)	(+)
8 hours	1	700°C	(-)	(+)
1 hour	2	750°C	(+)	(+)
1 hour	1	800°C	(+)	(-)
8 hours	1	800°C	(+)	(-)

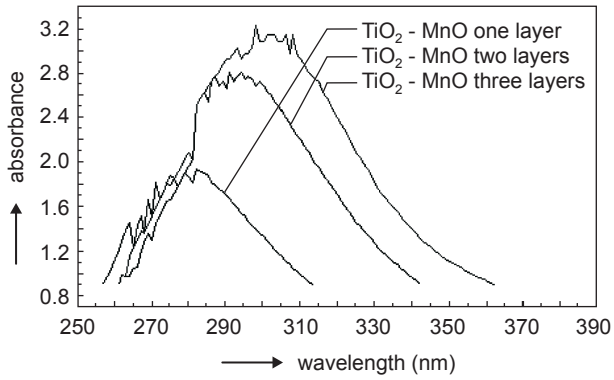


Figure 3. UV absorbance of TiO_2-MnO layers consisting of 1, 2 and 3 films (550°C, 1 hour) on the slide glass.

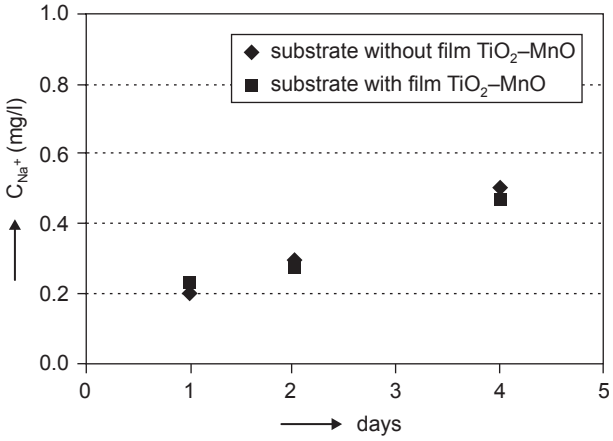


Figure 4. The time dependence of Na^+ concentration in demineralised water after corrosion of the sample with one TiO_2-MnO film (550°C, 1 hour) at 80°C.

increasing wavelength value. The value of refractive index apparently depends on the microstructure (mainly porosity) of the layers. Figure 6 should correspond to this but no corresponding reliable data of porosities were established to verify the assumption. The change of refractive index with the number of films may be complicated by the existence of more optical interfaces which might cause complicated interference phenomena.

Figure 7 shows the surface of TiO_2-MnO film with one coating. The size of single anatase crystals appears to be about 10-20 nm, also some aggregates are observed and the amount of the pores is high.

Figure 8 shows the surface of TiO_2-MnO film with two coatings. It is possible to observe the increase of the amount and size of the aggregates into the films. The layer with three subsequent coatings appears to be more uniform, without any aggregates and also without pores (figure 9).

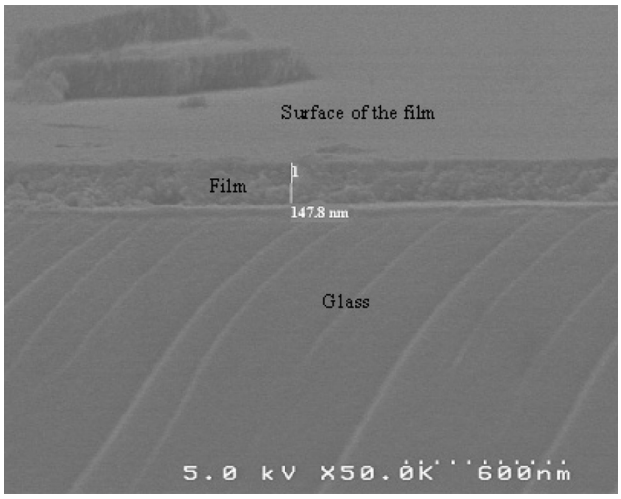


Figure 5a. SEM micrograph of the perpendicular section of TiO_2-MnO layer prepared by two subsequent depositions of a film on the slide glass (heating temperature 550°C, time 1 hour).

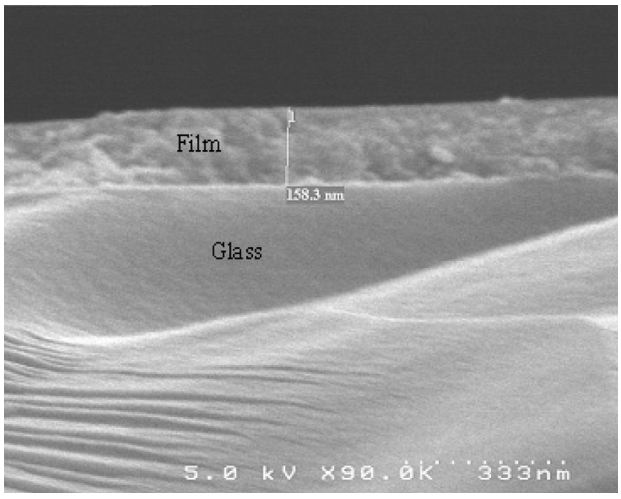


Figure 5b. SEM micrograph of the perpendicular section of TiO_2 MnO layers with three films on the slide glass (heating temperature 550°C, time 1 hour).

CONCLUSION

The optimal conditions for preparation of TiO_2-MnO gels from tetra-n-butyl-orthotitanate using sol-gel method and their deposition on soda lime glass by dip-coating technique were suggested and experimentally verified. Also parameters of formation of TiO_2-MnO layers on the glass substrate (temperature and time of drying and heating) were established with respect to the composition, adhesion and homogeneity of the layers. Thermo gravimetric study of TiO_2-MnO xerogels and their RTG analysis showed presence of anatase crystals starting from the temperatures of 550-600°C. The lowest temperature of anatase-rutile transition was found to be 700°C. The addition of Mn into the TiO_2 sol lowers the crystallization temperature as well as anatase-rutile transition temperature. From the spectrometric measurements it was found that the films are transparent in the visible region and show characteristic absorption in

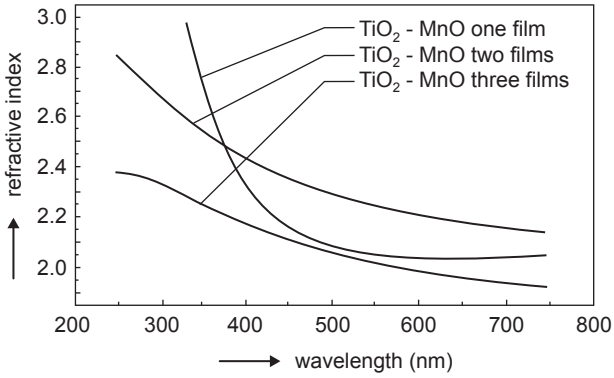


Figure 6. Refractive Index of TiO_2-MnO layers with different coatings number.

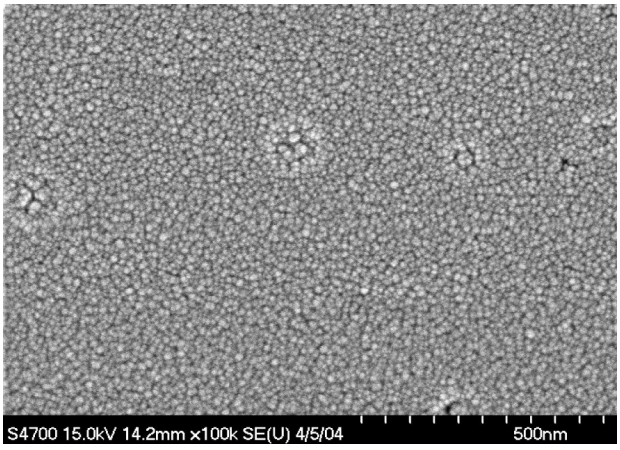


Figure 7. SEM micrographs of the surface of TiO_2-MnO layer with one coating at 550°C on the slide glass (heating temperature 550°C, time 1 h).

the wavelengths range of 275-306 nm. The width of the band absorption increases with the increasing film thickness. According to SEM micrographs and optical microscope examination, the TiO_2-MnO films are homogeneous especially if more consequent coatings are used for their preparation. The layers are not resistant against corrosion in warm water (80°C) and so do not protect the substrate against water corrosion.

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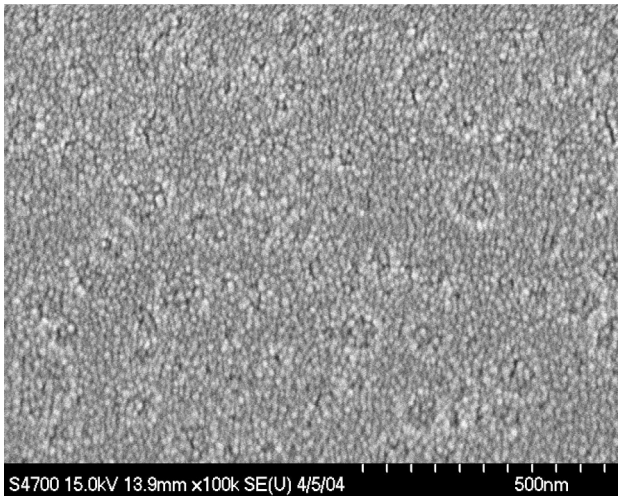

Figure 8. SEM micrographs of the surface of TiO_2-MnO layer with two coatings at 550°C on the slide glass (heating temperature 550°C, time 1 h).

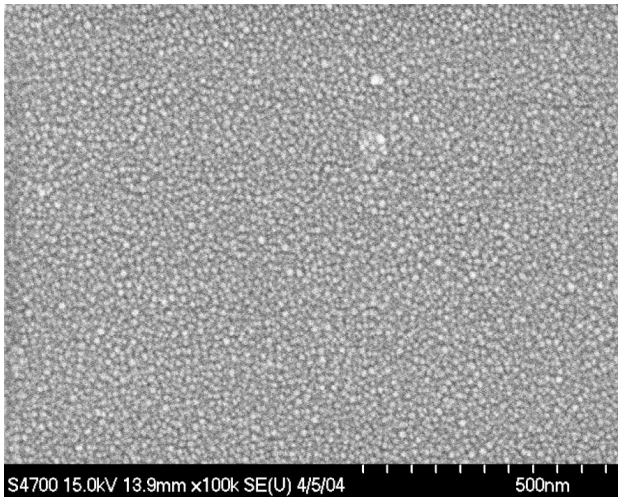

Figure 9. SEM micrographs of the surface of TiO_2-MnO layer with three coatings at 550°C on the slide glass (heating temperature 550°C, time 1 h).

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PŘÍPRAVA A CHARAKTERIZACE
TiO_2-MnO SOL-GEL VRSTEV NA SKLE

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Metodou sol-gel byly připraveny směsné oxidické vrstvy TiO_2-MnO za použití prekurzorů tetra-n-butyl-orthotitanátu a dusičnanu manganatého. Byly nalezeny optimální poměrné obsahy látek použitých pro přípravu solu a určeny podmínky sušení a finálního výpalu. Sol-gel vrstvy byly nanášeny metodou dip-coating a poté vypáleny na zvolenou teplotu v rozsahu 550-800°C. Pro sledování změn čerstvě připraveného xerogelu s teplotou byla použita DTA a TG analýza. Tato měření, spolu s RTG analýzou potvrdila přítomnost anatasu od teploty 550°C. Počínaje teplotou 700°C byl ve vrstvách detekován rovněž rutil. Spektrometrická měření ukázala, že vrstvy jsou transparentní ve viditelné oblasti spektra a vykazují charakteristickou absorbci s maximem v oblasti 275-306 nm. Šířka absorbčního pásu roste se zvyšujícím se tloušťkou vrstvy. Mikroskopická pozorování prokázala, že vrstvy jsou homogenní zvláště v případě vrstev získaných opakovaným nanesením více filmů. Tloušťka filmu byla 147 a 158 nm pro vrstvy získané opakovaným dvojím, resp. trojím nanesením. Index lomu vrstev závisí rovněž na počtu opakovaně nanášených filmů při jejich přípravě a pohybuje se v rozmezí od 1.9 do 2.9 podle vlnové délky světla.. Stanovením obsahu Na^+ iontů ve výluhu po korozi ve vodném statickém prostředí (80°C) bylo zjištěno, že tato hodnota je srovnatelná u vzorků s vrstvou a u vzorků s původním, nechráněným povrchem.