PREPARATION OF TiO_2 SOL-GEL LAYERS ON GLASS

LILIANA RODRIGUEZ PAEZ, JOSEF MATOUŠEK

Department of Glass and Ceramics, Institute of Chemical Technology Prague
Technická 5, 16628 Prague, Czech Republic

E-mail: rodrigul@vscht.cz

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TiO_2 thin films have been deposited onto glass substrates by sol-gel process using dip coating method. The coating solution was prepared by using tetra-n-butylorthotitanate precursor. The thermal transformation behaviour of the fresh xerogel was followed by thermal analysis and powder X-ray diffraction .The gels annealed at temperatures up to 350°C were examined by XRD and found to be amorphous. The diffraction peaks of anatase were found in gels annealed at 350°C or higher temperatures. The successive dense and homogenous films were optically characterized using UV-spectrophotometry. It was observed that the films were transparent in visible region and showed characteristic absorption in UV region.

INTRODUCTION

The sol-gel process is one of the most appropriate methods for the preparation of microporous and mesoporous oxide layers. It corresponds to an inorganic polymerisation, which starts from the mixture of precursors homogeneous at the molecular level [1]. The sol-gel method allows the preparation of catalytically active materials, which can be directly cast on supports at the sol stage. It is also used for the formation of various functional coatings, because of a large number of advantages such as easy coating of relatively large areas, accessibility of nanocrystalline materials and homogeneous multicomponent oxide films [2-4].

Titania (TiO_2) is a large band gap semiconductor with many interesting properties. It is transparent to visible light and has high refractive index (at λ = 550 nm, n = 2.54 for anatase or 2.75 for rutile). Titanium oxide thin films are widely used as optical and also protective coatings because of their excellent chemical stability, mechanical hardness and optical transmittance [15]. Sol-gel derived TiO_2 films are used as photocatalysts for purification and treatment of water and air [5,6], and as photoelectrodes in solar cells [7]. Other potential applications are supposed in optical and electrochromic devices [8,9] and electrical batteries [10]. Many attempts have been made to modify the physical, chemical and optical properties by mixing TiO_2 with oxides of other elements such as V [11], W [12,13] and Ce [14].

The aim of this work is to elaborate a reliable and reproducible method of preparation TiO_2 films on glass supports and to characterize some properties of those films.

Literature data on preparation and properties of TiO_2 layers

Titanium alcoxide have been usually used as the starting material for preparation of TiO_2 films. Gestel [18] used tetra-isopropoxide of titanium, which was hydrolysed at the temperature of 50°C in acid solution composed of 0.5 mol HNO_3 and stoichiometric amount of water. Nishide a Mizukami [19] used for the preparation of the sol the same alcoxide, which was heated for 1.5 hours in ethanol at the temperature of 80°C in a reflux device. Gryčová [17] used for the preparation of TiO_2 films tetra-n-butylorthotitanate (TbuT), which was dissolved in ethanol and hydrolysed in acid solution. Gouma [20] used tetra-isopropoxide of titanium (TTI) to prepare multi-layers using the spin-coating method. A hard film (800 nm), consisting of rutile was then formed by thermal treatment at the temperature of 600°C. It was found that the transformation of anatase to rutile depends of size of the initial anatase grains. The influence of temperature on the development of the crystalline form of TiO_2 films was detected by means of RTG analysis. It was found that anatase is formed by a temperature around 300°C while rutile was observed by the temperature of 500°C. The temperature of thermal treatment has an influence on the composition, morphology and properties of TiO_2 films. The thickness of films is decreasing and density, refraction index and the size of crystalline particles is increasing with rising temperature. The thickness of films is approximately of 1 nm to 1 mm. In general, a change of any preparation conditions or the components used can have serious influence on the properties of the films. It was found that corrosion resistance of the films against acids increases with the increase of content of anatase. The resistance of the films decreases with the increase of *pH* of corrosion solution. The mechanical and optical properties of films depend on the concentration and the type of alcoxide in the sol.

EXPERIMENTAL

The experimental work was focused on the investigation of the influence of components used for sol preparation on film properties. The materials used for the preparation of films are registered in the table 1 and the procedure of preparation is shown in the figure 1.

Dip-coating method was used to coat glass substrates by TiO_2 films. The equipment used for TiO_2 film preparation by means of dip coating method allowed to draw up the glass substrate by a defined velocity and to work under atmospheric pressure and normal air humidity. The evaporation of the solvent was controlled by atmospheric conditions. The subsequent destabilization of the sols by solvent evaporation leads to a gelation process and the formation of a transparent film [22]. The glass substrate for coating was cleaned with soap, nitric acid and distilled water. The speed of with-drawing of glass substrate (microscope slides 75×25×1 mm in size made of sodium-calcium glass) was around of 20 cm/min. The coatings were dried at 60°C for 30 minutes and then heated in a furnace at 450°C for 45 minutes in air atmosphere. The films were then transparent with good adhesion on glass substrates.

Table 1. Materials used for sol preparation.

compound	properties
tetra-n-butylorthotitanate (TbuT) $(CH_3(CH_2)_3O)_4Ti$	*M* = 340.36 g/mol $\rho_{20°C}$ = 1.00 g/cm_3 purity > 98%
ethanol C_2H_5OH	*M* = 46.06 g/mol $\rho_{20°C}$ = 0.789 g/cm^3
isopropanol $(CH_3)_2CHOH$	*M*= 60.1 g/mol $\rho_{20°C}$ = 0.785 g/cm^3
n-Butanol $CH_3(CH_2)_3OH$	*M* = 74.12 g/mol $\rho_{20°C}$ = 0.81 g/cm^3
chlorhydric acid HCl	*M* = 36.46 g/mol $\rho_{20°C}$ = 1.179 g/cm^3
acetic acid CH_3COOH	*M* = 60.05g/mol $\rho_{20°C}$ = 1.05 g/cm^3
acetylacetone $OC(CH_3)CH_2(CH_3)$ CO	*M* = 100.03g/mol $\rho_{20°C}$ = 0.97g/ cm^3
distilled water H_2O	*M* = 18.02 g/mol *pH* = 6.9 $\rho_{20°C}$ = 0.998 g/cm^3

The sequence of processes occurring during thermal treatment was followed by DTA and GTA (scanning rate of 10°C/min) using a 60 mg sample of gel powder prepared by drying at 60°C in air. Also XR diffraction analyses was used to identify crystalline phases present in powders prepared by drying of the gel at 60°C and by heating at different temperatures in air for 30 minutes. The optical absorption spectra of films on glass substrates were measured by UV spectrophotometer Shimadzu 1201 in the spectral range of 200 - 1200 nm.

RESULTS AND DISCUSSIONS

All films that were prepared using n-butanol solution showed little homogeneity on the substrate. The films that were prepared with ethanol or isopropanol solutions had good adhesion and homogeneity on the substrate.

UV-vis absorption spectra of films on glass are shown in figure 2. The films are transparent in visible region (380 - 780 nm) and show characteristic absorption in UV region at a wavelength of around 280 nm.

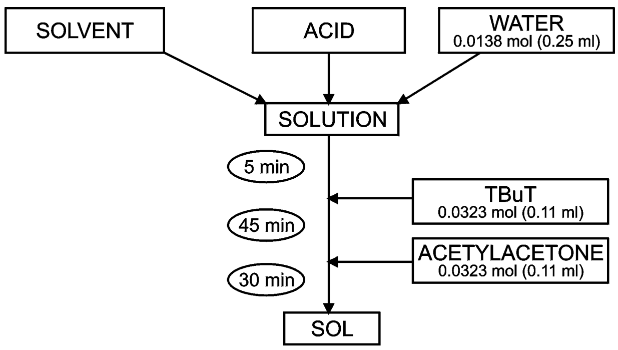

Figure 1. Scheme of sol preparation.

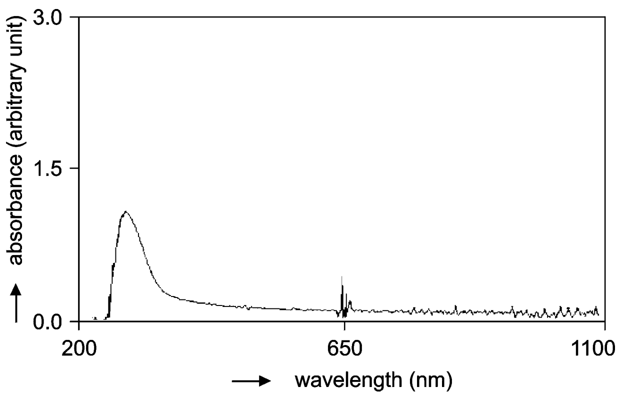

Figure 2. Absorbance spectrum of TiO_2 coating prepared using ethanol as a solvent and acetic acid as a catalyst.

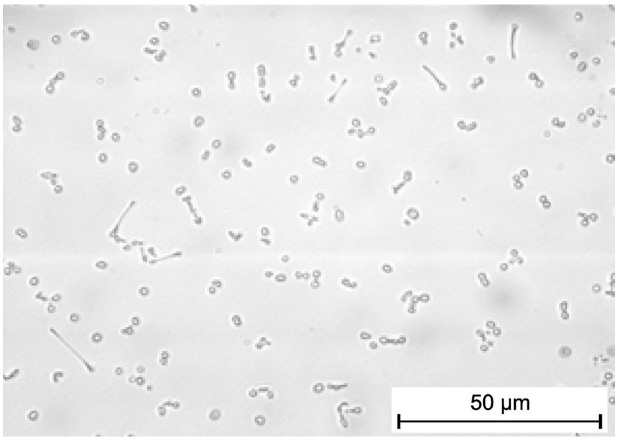

Figure 3. Typical optical microscope image of TiO_2 thin film prepared by heating at 450°C.

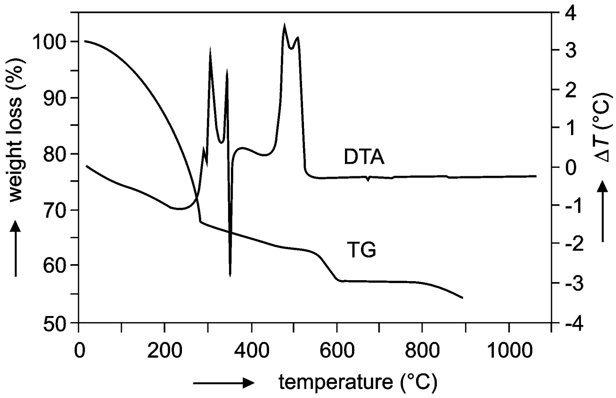

Figure 4. TG-DTA thermograms of TiO_2 xerogels.

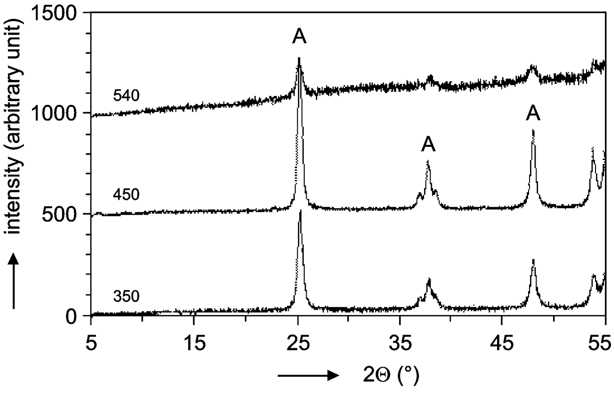

Figure 5. XRD diffraction patterns of TiO_2 gel heated at different temperatures.

The influence of solvent used for sol preparation on the absorbance spectra of films was found to be negligible. This was confirmed by using two different solvents - ethanol and isopropanol, which were giving layers with practically identical absorbance curve in the range of 200-1100 nm (see figure 2). The identical absorbance curve was also found, if the films were prepared using different acid catalysts (acetic or HCl water solution). The most important factor governing the absorbance spectra of the layers appeared to be final thermal treatment of the layers after layers deposition and drying. The layers treated at the temperature of 450°C have a little higher absorbance than those treated at 550°C and so the films are more translucent with rising temeperature of final thermal treatment [20]. Also refractive index of the glass samples with the TiO_2 layers was determined by ellipsometry. The refractive index value for the sample with ethanol as the solvent was found to be $n = 2.4$. In figure 3 the growth of crystals on the glass substrate is shown. TiO_2 thin films on glass substrates can be considered as aggregates containing TiO_2 in form of anatase particles. The anatase was observed starting from the temperature of 450°C probably as a result of a phase transition from an amorphous phase [15]. The size of particles was estimated to be around 1 µm.

The final temperature treatment of the layers seems to be the main factor influencing properties of the layers. Therefore, thermal analysis of the gels was used to detect processes in gels submitted to this procedure. DTA and TGA curves (figure 4) show that all processes in gels are finished up to the temperature of 600°C. Two exotermic peaks on DTA curve at the temperature interval of 300 - 340°C can be attributed to combustion of some organic substances. This process is not finished at those temperatures as it is documented by a strong exothermic peak in the temperature range of 450 - 550°C. An endothermic peak in the DTA curve observed at 350°C could correspond to a formation of anatase. Two main stages can be found on the TG curve.

The first one occuring in the temperature range from the room temperature to 300°C, results from the desorption or release of some substances in the gel such as the adsorbed water and ethanol. Starting from the 300°C the TGA curve decreases smoothly up to the temperature of 550°C. The loss of gel weight at the temperature range from 550 to 600°C possibly results from the desorption of the hydroxyl (OH^-) groups on the nanoparticles TiO_2 [25].

As it is seen from the figure 5, diffraction peaks of anatase were found in gels annealed at 350°C and higher temperatures.

The procedure used in this work for preparation of the layers is similar to the procedure used by Gryčová [17]. In comparison with Nishide[19] no reflux was used and layers were deposited only on glass substrate.

From the absorption spectrum curve (figure 2.), it is observed that the films are transparent in visible region and show characteristic absorption in UV region at a wavelength of around 305 nm. Negishi [24] indicated that the TiO_2 thin film calcined at 300°C is amorphous and the anatase peaks appeared not before the temperature of 400°C. The anatase to rutile phase transformation took place at temperatures of 600 - 800°C [24]. In the work of Kim [21] this anatase-to-rutile phase transformation occurred at 1000°C. In our work, the anatase peaks appeared at 350°C and the anatase to rutile phase transformation was not detected at the temperatures of thermal treatment used in this work. It may be seen, however, that the anatase peaks in figure 5 start to fade-out at 540°C.

CONCLUSION

The sol-gel procedure used for TiO_2 films preparation was examined with respect of sol composition and final gel film thermal treatment. It was found, that the solvent used for preparation of the sol have influence only on the homogeneity of the films but it is not important with respect to the optical absorbance of the film in the UV - region. The use of HCl or CH_3COOH during the preparation of sol has not significant influence on the absorbance of films. The films prepared on glass substrates show a significant absorbance in UV region of spectrum. The increase of the thermal treatment temperature increases slightly the translucent property of the films. The TiO_2 films consist of anatase particles.

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PŘÍPRAVA TiO_2 SOL-GEL VRSTEV NA SKLE

LILIANA RODRIGUEZ PAEZ, JOSEF MATOUŠEK

Ústav skla a keramiky,
Vysoká škola chemicko-technologická v Praze
Technická 5, 166 28 Praha 6 - Dejvice

Tenké vrstvy oxidu titaničitého připravené metodou sol-gel byly nanášeny na skelný substrát postupem dip-coating. Roztok pro nanášení byl připraven s použitím tetra-n-butoxytitanu jako prekurzoru. Chování čerstvě připraveného gelu při tepelném ohřevu bylo sledováno pomocí DTA, TGA a práškové rentgenové difrakční analýzy. Gely zahřáté na teplotu nižší než 350°C měly amorfní strukturu. Nad touto teplotou byly identifikovány difrakční píky anatasu. Sol-gel vrstvy byly nanášeny metodou dip-coating a u dostatečně homogenních vrstev byla měřena optická absorpce. Bylo zjištěno, že filmy jsou transparentní ve viditelné části spektra, vykazují charakteristickou absorbci v UV oblasti a jsou tvořeny částicemi anatasu.