

# Photodecomposition of Rhodamine B on TiO<sub>2</sub>/SiO<sub>2</sub> thin films prepared by sol-gel method

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Glasses showing catalytic effect have been of much interest recently because the catalytic layer is very effective in reducing of pollutants. The use of these glasses may bring reduction in cleaning costs. There are several methods of preparation of TiO<sub>2</sub> with good catalytic properties, but sol-gel technique offers an opportunity to enhance catalytic effect by precise optimization of the composition and microstructure of the layer. This study concerns optimization of the composition and preparation technology of catalytic layers based on SiO<sub>2</sub>–TiO<sub>2</sub> system. Catalytic effect was studied using Rhodamine B as a sensor. UV-VIS and photoelectron spectroscopy were the main research tools used in this study.

Keywords: *photocatalytic effect; titanium layer; sol-gel; Rhodamine B*

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## 1. Introduction

TiO<sub>2</sub> is the best candidate for photocatalytic application because of good chemical stability, non-toxicity and high photocatalytic activity. The photocatalytic properties of TiO<sub>2</sub> were discovered many years ago but since the discovery by Fujishima and Honda [1] showing that TiO<sub>2</sub> is able to split water, the number of research have grown exponentially. TiO<sub>2</sub> has been found to be the best photocatalyst in total destruction of many organic compounds in polluted wastewater [1–5]. The photodegradation properties of titanium oxide were utilized also in glass technology to produce self-cleaning glasses [6–10]. Organic pollutants decompose on thin layer of TiO<sub>2</sub> under UV radiation. Additionally, UV radiation induces hydrophilicity in the titanium layer, which helps to remove the decomposed pollutants [11, 12]. All crystallographic forms of TiO<sub>2</sub> have photocatalytic properties but the most effective is anatase. The band gap of anatase is 3.2 eV, which requires UV radiation ( $\lambda < 387$  nm) to transfer an electron from valence to conduction band. Although rutile has a lower value of band gap – 3.0 eV, which makes possible to use radiation close to visible re-

gion, its efficiency is lower due to higher rate of electron-hole recombination compared to anatase.

The main research activity is now focused on an improvement in the efficiency of photocatalyst, especially in the visible region. It can be realized by doping of TiO<sub>2</sub> with selected elements [13–15]. As early as in 1986 it was reported that the photocatalytic activity of TiO<sub>2</sub> can be enhanced by introducing SiO<sub>2</sub> [16]. The later publications confirm the positive effect of SiO<sub>2</sub> addition on TiO<sub>2</sub> activity [17–19]. Sol-gel method is the most convenient method of doping TiO<sub>2</sub> and is widely used in the preparation of TiO<sub>2</sub> in form of thin layer [20, 21].

In the present work, TiO<sub>2</sub>-SiO<sub>2</sub> transparent thin films were prepared on glass sheets using sol-gel method. The main aim of this work was to find an optimal ratio of TiO<sub>2</sub> to SiO<sub>2</sub>, from the photocatalytic activity point of view, as well as to establish the optimal conditions for their preparation. Rhodamine B was used as a catalytic activity probe.

## 2. Experimental procedure

### 2.1. Sol preparation

The sol solutions were prepared using tetraethyloorthosilicate [TEOS] and tetraethyloorthotitanate [TEOT], Sigma-Aldrich. Ethanol 95 % and 2-pro-

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Table 1. Chemical composition of the sols.

Symbol	TEOS [mol]	C <sub>2</sub> H <sub>5</sub> OH [mol]	TEOT [mol]	H <sub>2</sub> O [mol]	HCl [mol]	C <sub>3</sub> H <sub>8</sub> O [mol]
T	–	3	0.5	1.3	0.025	32.75
S	1	3		1.3	0.025	25.8
ST11	0.5	3	0.5	1.3	0.025	25.8
ST21	1	3	0.5	1.3	0.025	25.8
ST12	0.5	3	1	1.3	0.025	25.8

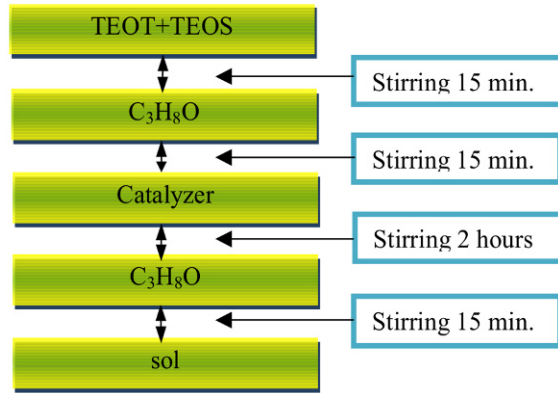


Fig. 1. Sol preparation procedure.

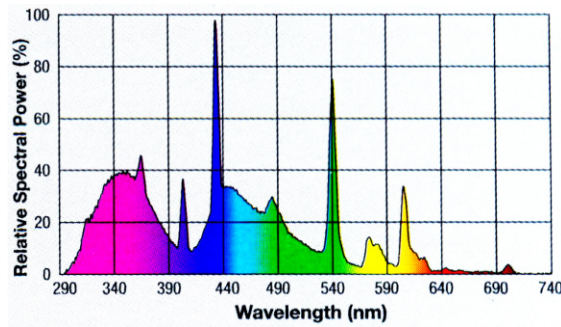


Fig. 2. Spectral characteristics of UV lamp.

panol (Polish Chemicals) were used as solvents. 1 M HCl (Polish Chemicals) was used to catalyze the hydrolysis reaction. Chemical composition of the sols is shown in the Table 1 while the preparation procedure is demonstrated in Fig. 1.

## 2.2. Preparation of thin films

Microscope slide glasses  $2.5 \times 7.5$  cm were used as a support. The glasses were first washed in distilled water dried and washed in ethanol. Both proce-

dures were carried out in ultrasonic bath. Thin film was prepared by dip-coating technique using different speeds of withdrawing. Samples were dried at room temperature and calcined at 500 °C for 30 min. Thicker films were produced by repeating the dipping procedure. The thickness of the films, estimated from ellipsometric measurements (PHE 102 ellipsometer from Angstrom Advance), was in the range of 120 – 800 nm for 1 and 6 coatings, respectively and varied with sol composition. Cauchy model was applied to evaluate the thickness of a sample.

## 2.3. Evaluation of photocatalytic activity

Photocatalytic activity of the thin film was evaluated on the base of changes in Rhodamine B peak area before and after UV exposure. Absorption spectra were measured with Jasco V-630 spectrometer. Rhodamine B solution was prepared by dissolving the dye in ethanol. The content of Rhodamine B in a solution was 0.5 %. The samples were coated with Rhodamine B solution using a dip-coating technique. A uniform and homogeneous layer of the dye was obtained. The dye-coated samples were irradiated with UV fluorescent lamp with 20 W power. The distance of the lamp from the sample surface was 15 cm and the irradiation was done in air. The spectral characteristics of the lamp is shown in Fig. 2. Photocatalytic activity is presented as a decrease in Rhodamine peak area expressed in %:

$$Pha = \frac{R_a - R_b}{R_a} \times 100 \quad (1)$$

where  $Pha$  is photocatalytic activity,  $R_b$  – Rhodamine peak area before UV exposure,  $R_a$  – Rhodamine peak area after UV exposure.

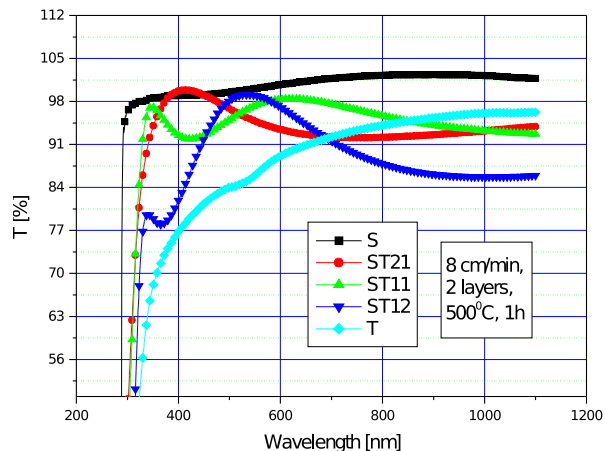


Fig. 3. Transmittance of the samples with the films prepared from the sols indicated in the legend of the figure.

## 2.4. Thin film characterisation

Surface compositions of the samples were estimated from XPS measurements using VSW spectrometer. Al K $\alpha$  200 W was used as an X-ray source. The spectra were calibrated on carbon C1s peak with binding energy  $E_b = 284.6$  eV [22, 23]. Curve fitting procedure was carried out using XPSPEAK 4.1 program (Raymunda W.M. Kwok, The Chinese University of Hong Kong). Quantity analysis was made using sensitivity factors published by Briggs and Seah [24].

## 3. Results and discussion

### 3.1. Optical properties

All thin films prepared from the sols are highly transparent. Transmittance spectra of the samples with a layer deposited on both sides of the glass at a rate of 8 cm/min and fired at 500 °C for 1 h, are shown in Fig. 3. The samples prepared from pure SiO<sub>2</sub> sol – “S” exhibit the highest transmittance. An increase in TiO<sub>2</sub> content makes the film more reflectant and leads to lower transmittance values. The lowest transmittance is observed in the case of “T” sol but is still higher than 90 %.

Refractive index of the films was established from ellipsometry measurements. The refractive index changes with wavelength, and in the case of “T”

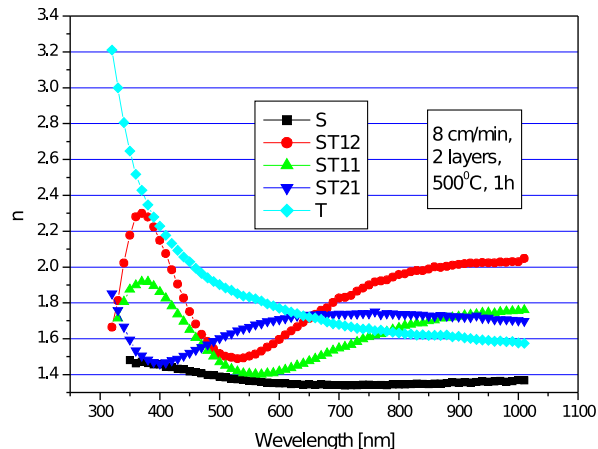


Fig. 4. Refractive index measured for the samples annealed at 500 °C for 1 h.

sample it ranges from 2.647 at 350 nm to 1.579 at 1000 nm (Fig. 4).

The value of  $n_D = 1.793$  is much lower than  $n_D = 2.488$  observed in the case of TiO<sub>2</sub> in polycrystalline anatase form, which is due to high porosity of the layer. The porosity estimated from the ellipsometric measurements is approximately by 40 % higher than that in bulk.

The high porosity of sample “T” may result from large amount of propanol used in the synthesis of this sol. An excess of propanol is necessary to prevent rapid condensation of TiO<sub>2</sub> particles. Pure SiO<sub>2</sub> sol, “S”, yields the layer with refractive index varying from 1.480 to 1.369 at 350 and 1000 nm, respectively, and  $n_D = 1.353$ . It is also lower than  $n_D = 1.458$ , observed in the case of pure SiO<sub>2</sub> glass. Porosity of “S” samples was assessed to be 20 %. The values of refractive index and porosity of the samples based on the mixed composition marked as “ST” are between those observed for “T” and “S” samples.

### 3.2. XPS results

Photoelectron spectroscopy was used to analyze surface composition and follow the changes in sodium content with annealing temperature. Ti2p region of “T” sample after 1 h, 500 °C annealing is shown in Fig. 5. The spectrum reveals Ti2p<sub>3/2</sub> peak at 458.0 eV and Ti2p<sub>1/2</sub> peak at 463.7 eV which correspond to characteristic binding energies of Ti, usu-

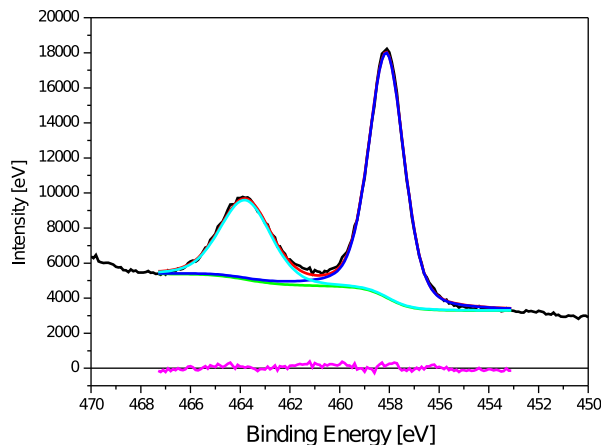


Fig. 5. Ti2p core level spectrum of the surface of the TiO<sub>2</sub> layer.

ally observed in TiO<sub>2</sub> [22, 23]. The binding energy of titanium has not changed with titanium content. Fig. 6 shows high resolution O 1s region measured for “S” (Fig. 6a) and “ST12” (Fig. 6b) samples. In case of the sample prepared from “S” sol, the oxygen region consists of two peaks originating from OH, and Si–O (Fig. 6a). The binding energy of oxygen coming from OH group bound to sodium and physisorbed oxygen is 530.1 eV.

The spectrum is dominated by the peak coming from oxygen connected with Si atoms with binding energy of 531.9 eV [25]. O1s region of “ST12” sample consists of three peaks associated to oxygen bound with titanium, silica and coming from molecular water as well as C–O group (Fig. 6b). Oxygen atoms surrounding titanium have the binding energy of 529.6 eV. Such binding energy is often reported for TiO<sub>2</sub> [26, 27].

The binding energy of oxygen connected with Si atoms amounts to 531.1 eV and is by 0.7 eV lower than in the case of “S” sample. Such value of binding energy is observed in case of zeolites [28].

The binding energy of Si2p changes with Ti content from 103.0 eV for “S” sample to 102.1 eV for “ST12” sample. The observed decrease in binding energy of Si2p is connected with phase separation and formation of TiO<sub>2</sub> crystal in amorphous SiO<sub>2</sub> matrix. Crystallization of TiO<sub>2</sub> in SiO<sub>2</sub> amorphous matrix was thoroughly studied and was confirmed to take place even at low temperatures [21].

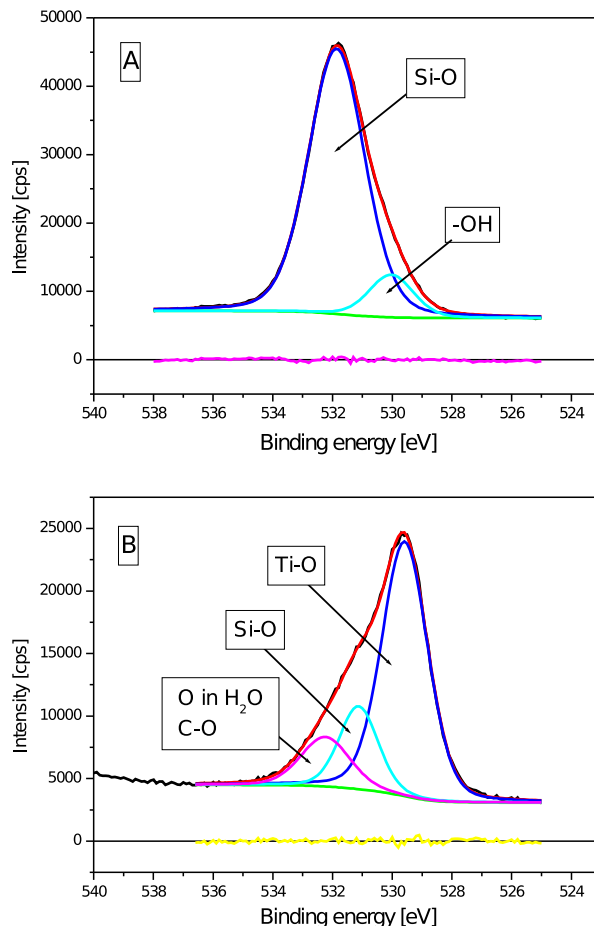


Fig. 6. O1s core level spectra of the “S” sample (A) and “ST12” sample (B).

### 3.3. Photocatalytic activity as a function of thickness and annealing time

The changes in photocatalytic activity were measured as a function of annealing time. The results are shown in Fig. 7.

The highest activity was observed in the case of “T” sample (Fig. 7b). Titanium film is the most sensitive to the annealing time, and its activity decreases rapidly with its elongation. The decrease in activity results mainly from TiO<sub>2</sub> crystals growth and the decrease in specific surface area of TiO<sub>2</sub>. The most desirable crystal size, from photo-activity point of view, is 20 – 40 nm [23], however, the elongated thermal treatment leads to the growth of bigger crystal. The optimal thermal treatment conditions for “T” sample were found to be 2 h annealing

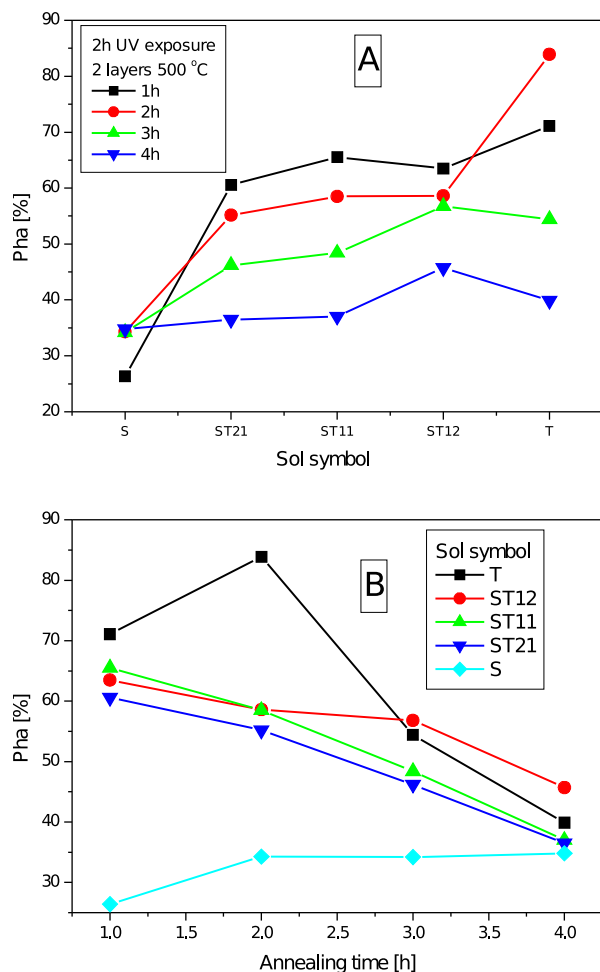


Fig. 7. Changes in photocatalytic activity as a function of annealing time for different sol compositions (A) and annealing temperatures (B). The points are connected to show the general tendency.

at 500 °C. For this conditions, the measured activity was higher than 80 % after 2 h UV radiation. “ST12” sample calcined for the time longer than 3 hours at 500 °C showed higher activity than “T” sample annealed at the same conditions, however, its total activity was lower than 60 %.

The samples with lower Ti content “ST11” and “ST21” showed the highest activity after 1h annealing but their activity decreased rapidly with annealing time. The decrease in activity in this case cannot be explained by TiO<sub>2</sub> crystal growth rate because the crystal growth rate is low in amorphous silica [21]. The observed activity decrease can be associated in this case with sodium content.

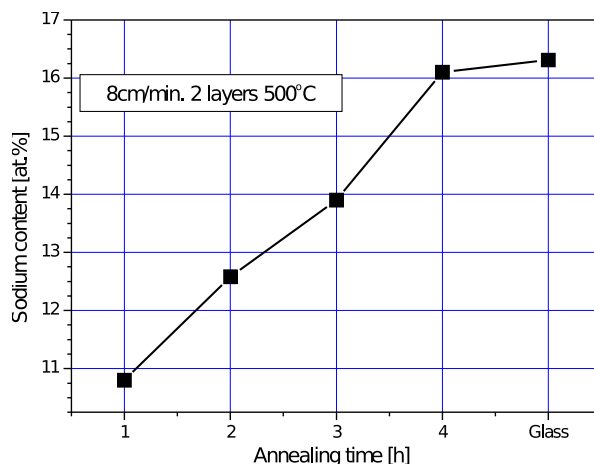


Fig. 8. Changes in sodium content at “T” sample with annealing time. The sample has deposited two TiO<sub>2</sub> layers, 275.46 nm thick. Sodium content at the glass surface is shown for comparison.

Sodium content on the surface is very important from at least three reasons: it can influence TiO<sub>2</sub> crystallization, it can modify photocatalytic properties of titanium layer and, in case when dyes are used as a catalytic probe, it can change the color of the dye due to local changes in Ph at the surface. Sodium diffuses from the glass through the catalytic layer during the film sintering process. We used photoelectron spectroscopy to follow the changes in sodium content on the surface due to sintering process. The results for “T” sample are shown in Fig. 8.

After four hour annealing at 500 °C, sodium content approaches the value observed for glass surface. This shows that sodium can have significant influence on the obtained results. Because of possible changes in Ph at the surface, the catalytic activity measurement using dyes should be performed in an atmosphere with controlled humidity.

As the role of sodium in photoactivity assessment is not fully recognized, we used a quartz glass as substrates to eliminate sodium influence on the results. The samples were prepared in the same manner and in the same conditions as before. Fig. 9 shows the results of measurements of photoactivity for the samples annealed for 3 h at 500 °C. It is clearly seen, that the best result *i.e.* ~50 % activity has been obtained for “T” sample while the catalytic efficiency for “ST12” composition, is only



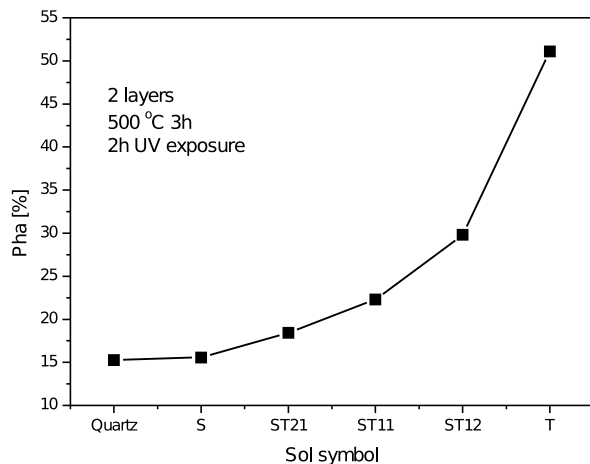


Fig. 9. Photoactivity after 2 h UV exposure for two layers of thin film deposited on a quartz substrate. The points are connected to visualize the tendency.

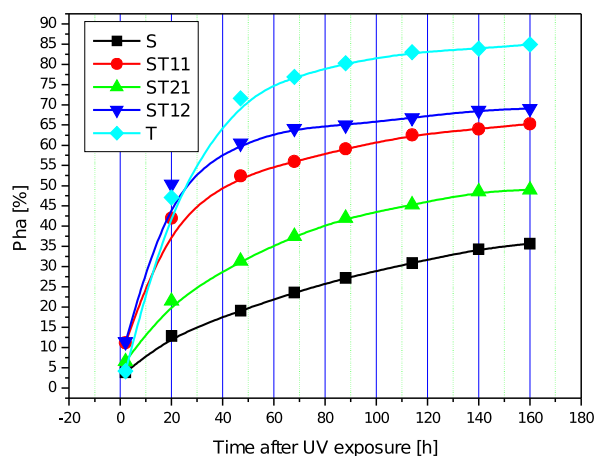


Fig. 10. Photocatalytic activity as a function of time after 2 h UV exposure.

30 %. The activity decreases rapidly with decreasing concentration of titanium in the sol. This confirms the observation that the higher activity of the sample "ST12" in comparison to the sample "T", measured for the samples prepared previously on the glass slides, resulted from sodium present in the layer. Most probably, sodium led to an increase in rutile phase content in "T" sample during annealing.

### 3.4. Darkroom behavior

Degradation of Rhodamine B was also observed several hours after the UV was switched off. The

samples after 2 h UV radiation were kept in the darkness and the changes in Rhodamine absorption peak were measured in selected intervals of time. Fig. 10 shows how the activity changes with time after 2 hour UV exposure. The most active are "T" layers. Degradation reaches 85 % after 160 h. The samples with the lower content of Ti show lower degradation activity. The observed behavior is connected with catalytic properties of  $\text{TiO}_2$ . Active species are created during photocatalytic process and react with the Rhodamine film. The active species concentration can be high as the layers prepared using sol-gel method exhibit high porosity.

The porosity has another positive aspect as water vapor, essential in photocatalytic process, can cumulate in the pores. After UV exposure the water decomposes to form different active species such as oxygen radicals, ozone and hydrogen. These radicals decompose Rhodamine leading to the color change. The diffusion process of active species through the Rhodamine film is slow, so we observed dark-room behavior. Such a behavior of a sol-gel prepared photocatalytic film is very useful from practical point of view because degradation of contaminants is possible even during cloudy days.

## 4. Conclusions

Thin films of  $\text{SiO}_2/\text{TiO}_2$  with different content of  $\text{SiO}_2$  and  $\text{TiO}_2$  were prepared. The best photocatalytic properties exhibited the  $\text{TiO}_2$  film. Photocatalytic activity of the sample was influenced significantly by the time of annealing. The best results were obtained as a result of 1 – 2 h annealing at 450 °C. All compositions showed long-term darkroom degradation activity but the highest efficiency was recorded for the samples prepared from "T" sol. Sodium content in the film can influence significantly the results of rhodamine B photodecomposition so the measurements should be carried out at controlled humidity atmosphere.

## References

- [1] FUJISHIMA A., HONDA K., *Nature*, 238 (1972), 37.
- [2] DOMINGUEZ C., GRACIA J., PEDRAZ M.A., TORRES A., GALAN M.A., *Catalysis Today*, 40 (1998), 85.
- [3] HERMAN J.M., *Catalysis Today*, 53 (1999), 115.

- [4] HIDAKA H., ZHAO J., *Colloids and Surfaces*, 67 (1992), 165.
- [5] KANIOU S., PITRAKIS K., BARLAGIANNI I., POULIOS I., *Chemosphere*, 60 (2005), 372.
- [6] AEGERTER M.A., ALMEIDA R., SOUTAR A., TADANAGA K., YANG H., WATANABE T., *J. Sol-Gel Sci. Technol.*, 47 (2008), 203.
- [7] KOMINAMI H., TAKADA Y., YAMAGIWA H., KERA Y., INOUE M., *J. Mater. Sci. Letter*, 15 (1996), 197.
- [8] SOPYAN I., WATANABE M., MURASAWA S., HASHIMOTO K., FUJISHIMA A., *J. Photochem. Photobiol. A: Chem.*, 98 (1996), 79.
- [9] KIM D.H., ANDERSON M.A., *J. Photochem. Photobiol. A: Chem.*, 94 (1996), 221.
- [10] PERAL J., OLLIS D.F., *J. Catal.*, 136 (1992), 554.
- [11] LUO Z.K., SONG L.X., LI M., LIU J.H., CAI J.H., *Inorg. Mat.*, 19 (2004), 1397.
- [12] LUO H.Y., LUO Z.K., CAI H.H., LIU J.H., ZHANG P.X., LIANG X., REN X.Z., *Key Eng. Mat.*, 336–338 (2007), 1901.
- [13] STIR M., NICULA R., BURKEL E., *J. Eur. Ceram. Soc.*, 26 (2006), 1542.
- [14] TIAN X.B., WANG Z.M., YANG S.Q., LUO Z.J., FU R.K.Y., CHU P.K., *Surf. Coat. Technol.*, 201 (2007), 8606.
- [15] ZHANG H.J., WEN D.Z., *Surf. Coat. Technol.*, 201 (2007), 5720.
- [16] ANPO M., NAKAYA H., KODAMA S., KUBOKAWA Y., *J. Phys. Chem.*, 90 (1986), 1633.
- [17] ANDERSON C., BARD A.J., *J. Phys. Chem. B*, 101 (1997), 2611.
- [18] ANDERSON C., BARD A.J., *J. Phys. Chem. B*, 99 (1995), 9882.
- [19] XU Y., ZHENG W. AND LIU W., *J. Photochem. Photobiol. A. Chem.*, 122 (1999), 57.
- [20] ALMEIDA R.M., MARQUES M.I.B., ORIGNAC X., *J. Sol-Gel Sci. and Technol.*, 8 (1997), 293.
- [21] YU J., YU J.C., ZHAO X., *J. Sol-Gel Sci. and Technol.*, 24 (2002), 95.
- [22] WAGNER C.D., RIGGS W.M., DAVIS L.E., MOULDER J.F., MUILENBERG G.E., in *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer, 1976.
- [23] GE L., XU M., *J. Sol-Gel Sci. and Technol.*, 43 (2007), 1.
- [24] BRIGGS D., SEACH M.P., in *Practical Surface Analysis*, J. Wiley and Sons, NY, 1983.
- [25] DE ANGELIS B.A., RIZZO C., CONTARINI S., HOWLETT S.P., *Appl. Surf. Sci.*, 51 (1991), 177.
- [26] HURAVLEV JU.F., KUZNETSOV M.V., GUBANOV V.A., *J. Electron Spectroscopy and Related Phenomena*, 38 (1992), 169.
- [27] CARDINAUD CH., LEMPERIERE G., PEIGNON M.C., JOUAN P.Y., *Appl. Surf. Sci.*, 68 (1993), 595.
- [28] BARR T.L., *J. Phys. Chem.*, 10 (1990), 760.

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