

Photocatalytic properties of Ti–V oxides thin films

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In this work, the photocatalytic properties of Ti–V oxides thin films with 19 and 23 at.% of vanadium addition have been outlined. The films were deposited by the high energy reactive magnetron sputtering method. X-ray photoelectron spectroscopy measurements were done in order to determine the chemical composition and binding energy of the elements on the samples surface. Additionally, based on wettability measurements, the water contact angles were evaluated and were equal to *ca.* 94° and 55° for thin films with 19 and 23 at.% of V, respectively. This testifies about hydrophilic and hydrophobic properties, respectively. Photoactivity of thin films was determined by percent decomposition of phenol for 5 hours during UV–vis radiation exposure. The highest photocatalytic activity of 6.2%/cm² was obtained for thin films with 19 at.% of V. It has been found that an increase in V amount in Ti–V oxides thin films to 23 at.% results in lowered to 3%/cm² photocatalytic activity.

Keywords: titanium dioxide (TiO₂), thin films, magnetron sputtering, vanadium, photocatalysis.

1. Introduction

One of the most often used materials with high photocatalytic activity is titanium dioxide (TiO₂) [1]. TiO₂ has many advantages, like excellent chemical, thermal and mechanical stability. It is also known as a low-cost and non-toxic material [2–4]. TiO₂ can be applied in various applications [1]. TiO₂ exhibits excellent optical transparency in a wide wavelength range and high refractive index [5]. Due to its wide band gap (3.2 eV [1]), it can use only a small portion of UV radiation that can be absorbed and as a result, the efficiency of photocatalytic process is limited [6]. To shift the absorption edge of TiO₂ from UV to the visible spectral range and simultaneously to reduce the recombination rate of excited electrons and holes, doping of TiO₂ with metal ions has been applied [7, 8]. Transition elements like Cr, Mo, W or V have been frequently used as dopants to TiO₂ matrix, because of their high absorption in the visible region, which in turn can improve photocatalytic activity [9–11]. As it is

concluded from the reports [12, 13], among the transition metal ions, the vanadium element is the most often used as a dopant, because it can increase carrier lifetime and also extend the absorption range of TiO_2 . In addition, vanadium doping may reduce the TiO_2 band gap even to 2.5–2.7 eV [14] and promote the crystal growth and phase transformation of TiO_2 [15]. CHOI *et al.* showed that only elements like V and Fe can raise the TiO_2 activity, because they possess unoccupied energy levels in the conduction band [7]. Therefore, many research groups have prepared V-doped TiO_2 and studied its photocatalytic properties. KLOSEK and RAFTERY reported that the V-doped TiO_2 can photodegrade ethanol under the illumination of visible light [11]. WANG and DOREN found that some spin-polarized gap states, also formed in the gap after V-doping, besides the broadening of the conduction band, narrow its band gap [16].

The aim of the present study is to evaluate the effects of vanadium addition to TiO_2 matrix on structure, wettability and photocatalytic activity of thin films prepared by the reactive magnetron sputtering method. On the basis of previous works [17, 18], the amount of V dopant was selected in order to compare photocatalytic activity of two thin films with different structural properties.

2. Experimental procedure

Mixed Ti–V oxides thin films were deposited on Corning (7059) glass and silica substrates with different concentration of V dopant using the high energy reactive magnetron sputtering (HERMS) method [19, 20]. Mosaic target consisting of V metallic foils located on Ti target was used to obtain Ti–V thin oxide films. The original part of the conducted work is that the sputtering was carried out applying oxygen as the only reactive and working gas instead of typical oxygen–argon mixture. Plasma pressure was kept below 0.1 Pa. Furthermore, the magnetron source was powered in a unipolar mode with 165 kHz sinusoidal pulses.

The content of V amount was analyzed using an energy dispersive spectrometer (Noran Vantage) and the concentration in two sets of prepared samples was 19 and 23 at.%. To determine the thickness of prepared films, a Taylor Hobson TalySurf CCI Lite optical profilometer was used, and it was equal to 334 and 360 nm for thin films with 19 and 23 at.% of V, respectively.

Crystal structure of prepared thin films was characterized by X-ray diffraction (XRD) method with the aid of DRON-2 powder diffractometer with Fe-filtered $\text{Co K}\alpha$ source.

The optical properties of the Ti–V oxides were measured at room temperature by Ocean Optics spectrophotometer. The transmission spectra were recorded in the range of 300–1000 nm.

Chemical states of the elements on the surface were studied by X-ray photoelectron spectroscopy (XPS). Experiments were performed with the aid of Specs Phoibos 100 MCD-5 (5 single channel electron multiplier) hemispherical analyzer in ultra-high vacuum conditions using Specs XR-50 X-ray source with $\text{Mg K}\alpha$ (1253.6 eV) beam.

The surface wettability of the thin films was evaluated by contact angle measurement of deionized water under room temperature and daylight illumination. The measure-

ment was carried out with a computer controlled CAM 200 goniometer system manufactured by KSV Ltd. The experiment was repeated five times and the average value was presented.

The photocatalytic behaviour of the films was investigated through photodegradation of phenol. The photocatalytic setup consisted of a UV–vis light source (6×20 W Phillips lamps with the following intensity of UV and vis radiation: 183 W/m^2 and 167 W/m^2 , respectively), cylindrical reservoir, which contained 100 ml of solution with the phenol concentration of 10 mg/l. Solution was prepared by dissolving the appropriate quantity of pure phenol in distilled water. To avoid the heating of the solution, the reaction temperature was controlled by circulation of water through the jacket at constant temperature (*ca.* 15°C). All experiments were done under agitation with a magnetic stirrer operating at 500 rpm in order to provide a good mixing of the suspension. No external oxygen supply was used. The phenol concentration was calculated from the absorption peak at 270 nm by means of a calibration curve. After 30 minutes of premixing at constant temperature, lights were switched on to initiate the reaction. To determine the change in phenol concentration, samples of phenol solutions were withdrawn regularly every 60 minutes for 5 hours from the reactor. The radiation exposure and photocatalytic reaction lasted for 5 hours. The final transparent solution was poured into a quartz cuvette and analyzed by UV–vis spectrophotometer.

3. Results and discussion

The XRD patterns (Figs. 1–3) show that the crystal structure of prepared Ti–V oxide thin films depends on the vanadium amount incorporated into the films. In case of 19 at.% of V, no characteristic peaks of titanium dioxide or vanadium oxides were detected (Fig. 1). This indicates on amorphous behaviour. When the amount of vanadium increases to 23 at.%, the nanocrystalline structure of V_2O_5 with crystallites size of 32.4 nm, calculated according to the Scherrer's formula, has been observed (Fig. 2a). AFM images of studied Ti–V oxide thin films have been shown in Figs. 2a

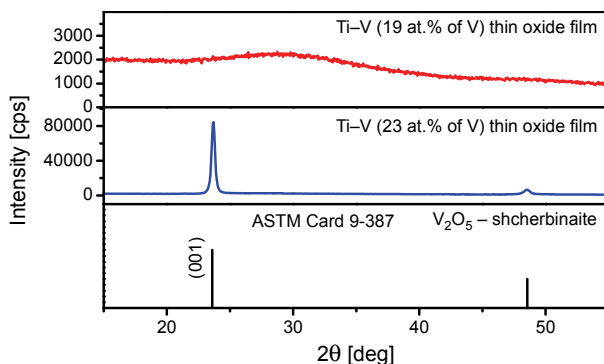


Fig. 1. XRD measurements of Ti–V oxides according to the standard pattern for V_2O_5 phase [21].

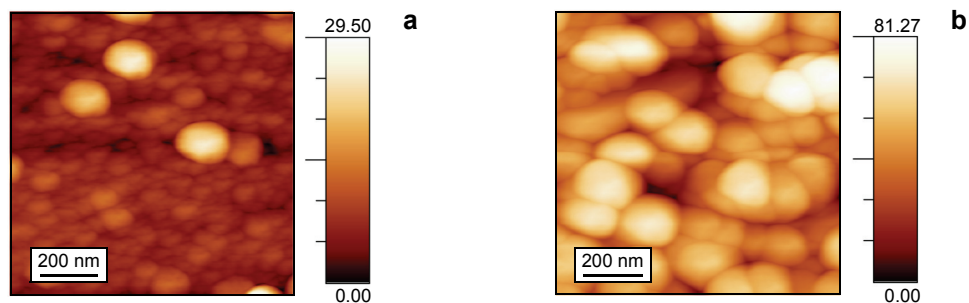


Fig. 2. AFM images of Ti–V oxides with 19 at.% of V (a) and 23 at.% of V (b).

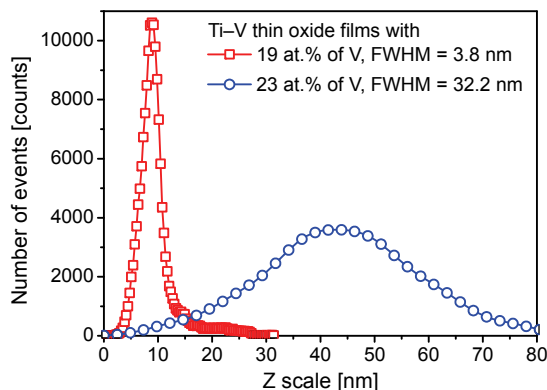


Fig. 3. The height distribution of grain size in Z direction.

and 2b. The investigation has revealed densely packed structure and homogenous surface in both cases. Grains visible in the images might be composed of several smaller crystallites. The analysis of AFM images has shown that RMS surface roughness is *ca.* 3.6 and 14.4 nm for Ti–V oxides with 19 and 23 at.% of V, respectively. Height distribution of grain size in Z direction has shown that in case of Ti–V oxide with 23 at.% of V the film is more diversified (Fig. 3).

To determine the distribution and chemical states of the V at the Ti–V oxide surface, XPS characterization has been performed. In Figures 4–6 the XPS Ti2*p*, V2*p* and O1*s* core level spectra of the fabricated thin films have been presented. The position of Ti2*p* doublet and separation of 5.5 eV and 5.9 eV for Ti–V (19 at.% of V) and Ti–V (23 at.% of V) thin films, respectively, between the Ti2*p*_{3/2} and Ti2*p*_{1/2} peaks indicate the Ti⁴⁺ oxidation state (Figs. 4a and 4b). This testifies about TiO₂ formation [22]. The V2*p*_{3/2} photoelectron peaks appear at 517.2 eV and 517.1 eV for the Ti–V (19 at.% of V) and Ti–V (23 at.% of V) films, respectively. This indicates on the appearance of V⁵⁺ species in the thin film and testifies about V₂O₅ presence. Furthermore, in obtained V2*p* XPS spectra (Figs. 5a and 5b), except V2*p*_{1/2} and V2*p*_{3/2}, two additional satellites can be observed at 519.5 eV, 521.6 eV for Ti–V (19 at.% of V) and at 519.2 eV, 521.6 eV for Ti–V (23 at.% of V).

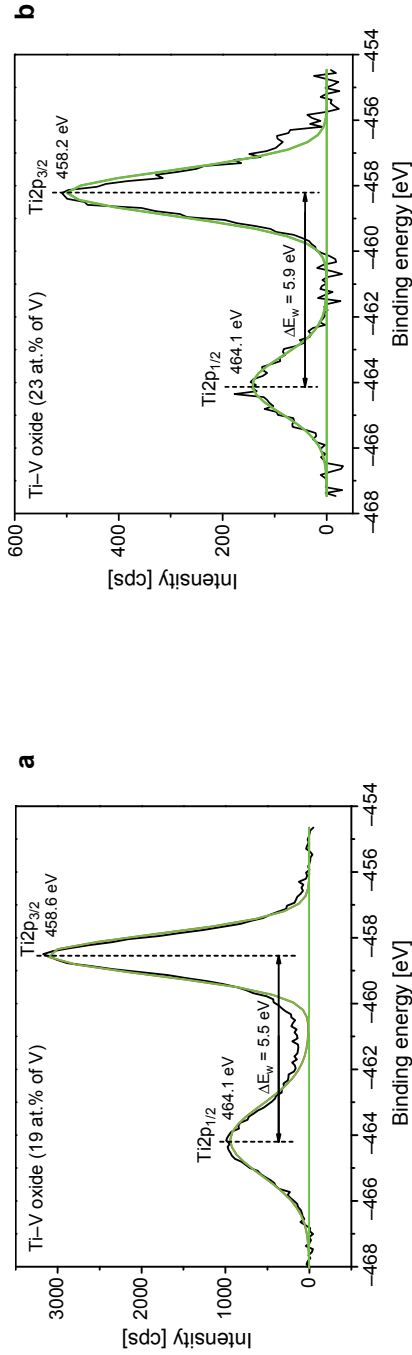


Fig. 4. XPS spectra of Ti2p core levels for Ti-V (19 at.% of V) (a) and Ti-V (23 at.% of V) (b) oxide thin films.

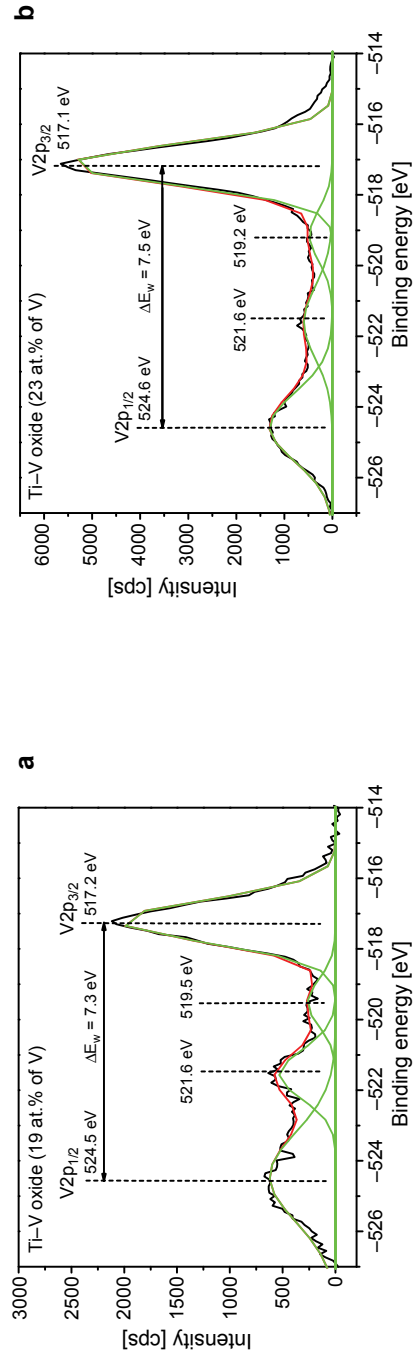


Fig. 5. XPS spectra of V2p core levels for Ti-V (19 at.% of V) (a) and Ti-V (23 at.% of V) (b) oxide thin films.

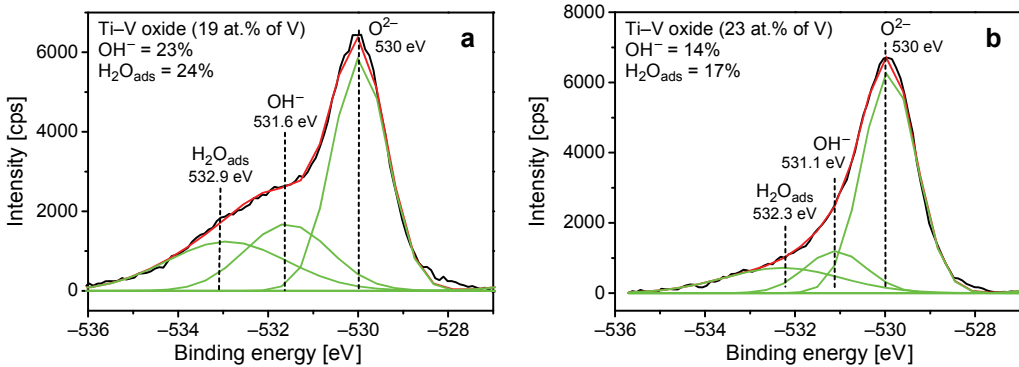


Fig. 6. XPS spectra of O1s core levels for Ti-V (19 at.% of V) (a) and Ti-V (23 at.% of V) (b) thin films.

In case of O1s oxidation state, the received results show the presence of hydroxyl radicals ($\bullet\text{OH}$) and water molecules (H_2O) on the thin films surface (Fig. 6). Hydroxyl radicals are formed on the surface of Ti-V oxides by reaction of holes in the valence band with adsorbed H_2O , hydroxide or surface titanol groups ($>\text{TiOH}$) [23]. The presence of TiOH groups indicates hydrophilicity [24], which decreases with an increase in V ion components on the surface.

T a b l e 1. Contact angle and critical surface tension of Ti-V with different amount of vanadium.

Thin oxide film	Vanadium amount [at.%]	Contact angle [deg]	Critical surface tension [mN/m]
Ti-V	19	93.9±2.8	10.2
	23	55.0±3.6	19.5

In Table 1 the values of a contact angle of Ti-V oxide thin films have been presented. This higher contact angle was obtained for Ti-V oxide thin film with 19 at.% of vanadium, which reveals hydrophobic properties. In case of Ti-V oxide thin film with 23 at.% of V, the contact angle has much lower than 90° and the thin films were hydrophilic. Such results can be connected with smaller roughness of Ti-V oxide thin film with 19 at.% of V in comparison to 23 at.% of V. Critical surface tension increased for a thin film with an increase in vanadium amount to 23 at.% and it was equal to 19.5 mN/m in comparison to 19 at.% with 10.2 mN/m. This indicates that Ti-V oxide thin films with 19 at.% of V have about two times less wettable surface than Ti-V oxide thin films with 23 at.% of V. It is likely that the critical surface tension also depends on roughness of measured samples surface. The lower value was obtained for an amorphous thin film with RMS of 3.6 nm.

The optical transparency of Ti-V oxide thin films deposited on SiO_2 substrates was determined on the basis of transmission spectra presented in Fig. 7a. In comparison to undoped TiO_2 , which transmission coefficient (T_λ) reaches *ca.* 80% in the visible spectral range [25], the addition of vanadium decreases the transparency level only for

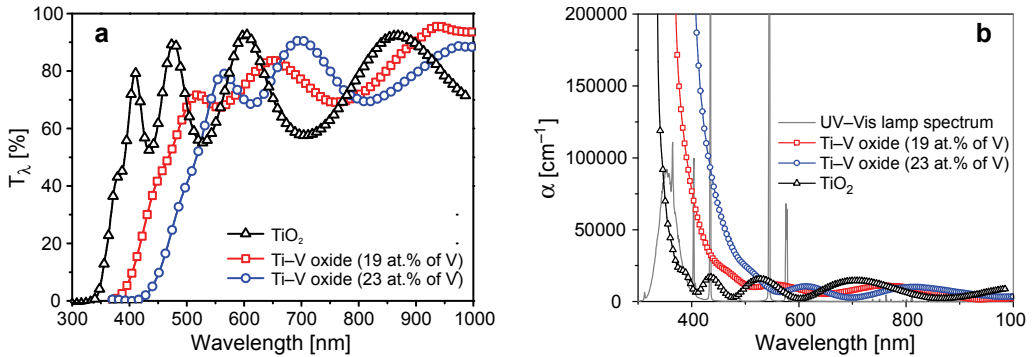


Fig. 7. Optical transmission (a) and absorption spectra (b) of TiO_2 and Ti–V oxide thin films with different amount of vanadium compared to the spectrum intensity of UV–vis lamp.

several percents. However, the measured films still reveal high transparency in considered spectral range and the average T_λ was *ca.* 73% for Ti–V oxide thin films. Additionally, based on optical transmission spectra, the cut-off wavelength has been estimated. It is equal to 380 and 430 nm for the Ti–V (19 at.% of V) and Ti–V (23 at.% of V) oxide thin films, respectively. In Figure 7b absorption spectra for TiO_2 and Ti–V oxides thin films have been presented in comparison to the UV–vis lamp spectrum, which was used during photocatalysis investigation. Absorption edge for Ti–V oxides is shifted towards longer wavelengths as compared to TiO_2 . Thin films compounds of Ti and V oxides can absorb more light in near UV and short wavelength part of visible light, what should result in their better photocatalytic activity than TiO_2 .

The photocatalytic activity of deposited thin films was determined based on phenol decomposition results. Photocatalytic reactions were conducted for 5 hours under UV–vis light. Figure 8 shows the influence of V amount on the photocatalytic activity of the Ti–V oxide thin films, defined as percentage phenol losses in a time function. By the reason of a small sample size of approximately 1 cm^2 , the phenol decomposition was estimated as $\%/ \text{cm}^2$. According to the results of phenol decomposition, thin films

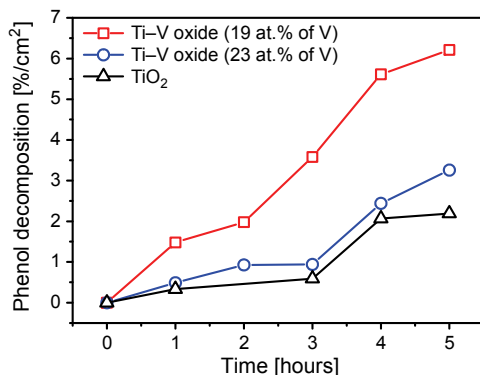


Fig. 8. Phenol decomposition of Ti–V oxide thin films with different amount in time.

with 19 at.% of V have higher photocatalytic activity than thin films with 23 at.% of V. It can be found that the photoactivity of Ti–V (19 at.% of V) is *ca.* 6%/cm², while for Ti–V (23 at.% of V) is equal to *ca.* 3%/cm². Obtained results are unique, because usually more efficient catalytic process proceeds for samples with crystalline structure, as described by EUFINGER *et al.* [26], while Ti–V (19 at.% of V) thin film reveals an amorphous phase according to XRD measurements. In comparison to powders, which have active surface area of about 50–200 m², the decomposition of phenol in case of Ti–V oxides thin film is high.

Based on XPS results, we assume that the sample with 19 at.% of vanadium has a better photocatalytic activity, due to the presence of larger amount of TiO₂ on the surface of the thin film. In the sample consisting of 23 at.% of vanadium, the surface was mostly covered by V₂O₅ particles what justify the lower photoactivity in comparison to Ti–V oxide (19 at.% of V). Moreover, the surface of Ti–V oxides thin film with 19 at.% of vanadium reveals higher quantity of OH radicals and H₂O molecules, which can also be connected with the higher photoactivity. We assume that Ti–V oxides thin films exhibit better photocatalytic activity in comparison to TiO₂, because such coatings can absorb more UV and also part of visible light and therefore photocatalysis is more effective.

4. Conclusions

Ti–V oxide thin films with different amount of vanadium have been prepared by the HERMS method. The XRD patterns exhibited the amorphous nature for Ti–V oxide with 19 at.% of V and nanocrystalline V₂O₅ phase for Ti–V oxide thin film with 23 at.% of V. Ti–V thin films have the absorption edge shifted into visible range as compared to undoped TiO₂. The XPS results showed more OH groups and H₂O molecules adsorbed for the sample with 19 at.% of vanadium. This is also confirmed by the photoactivity measurements. The contact angle investigation reveals hydrophobic behaviour for Ti–V oxide with 19 at.% of V and hydrophilic behaviour for Ti–V oxide with 23 at.% of V. The better photocatalytic activity has been obtained for amorphous thin film.

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References

- [1] CARP O., HUISMAN C.L., RELLER A., *Photoinduced reactivity of titanium dioxide*, Progress in Solid State Chemistry **32**(1–2), 2004, pp. 33–177.

- [2] XIAOBO CHEN, MAO S.S., *Titanium dioxide nanomaterials: synthesis, properties, modifications and applications*, Chemical Review **107**(7), 2007, pp. 2891–2959.
- [3] XUXU WANG, WENHAO LIAN, XIANZHI FU, BASSET J.-M., LEFEBVRE F., *Structure, preparation and photocatalytic activity of titanium oxides on MCM-41 surface*, Journal of Catalysis **238**(1), 2006, pp. 13–20.
- [4] JIAGUO YU, GUOHONG WANG, BEI CHENG, MINGHUA ZHOU, *Effects of hydrothermal temperature and time on the photocatalytic activity and microstructures of bimodal mesoporous TiO₂ powders*, Applied Catalysis B: Environmental **69**(3–4), 2007, pp. 171–180.
- [5] WANG W., HAO H., *Design of broadband and wide-angle antireflection for solar cells*, Chinese Optics Letters **8**, 2010, pp. 35–37.
- [6] LINSEBIGLER A.L., GUANGQUAN LU, YATES J.T., *Photocatalysis on TiO₂ surfaces: principles, mechanisms and selected results*, Chemical Review **95**(3), 1995, pp. 735–758.
- [7] CHOI W., TERMIN A., HOFFMANN M.R., *The role of metal ion dopants in quantum-sized TiO₂: correlation between photoreactivity and charge carrier recombination dynamics*, Journal of Physical Chemistry B **98**, 1994, pp. 13669–13679.
- [8] YAMASHITA H., HARADA M., MISAKA J., TAKEUCHI M., IKEUE K., ANPO M., *Degradation of propanol diluted in water under visible light irradiation using metal ion-implanted titanium dioxide photocatalysts*, Journal of Photochemistry and Photobiology A: Chemistry **148**(1–3), 2002, pp. 257–261.
- [9] JINKAI ZHOU, TAKEUCHI M., ZHAO X.S., RAY A.K., ANPO M., *Photocatalytic decomposition of formic acid under visible light irradiation over V-ion implanted TiO₂ thin film photocatalysts prepared on quartz substrate by ionized cluster beam (ICB) deposition method*, Catalysis Letters **106**(1–2), 2006, pp. 67–70.
- [10] IKETANI K., REN-DE SUN, TOKI M., HIROTA K., YAMAGUCHI O., *Sol-gel-derived V_xTi_{1-x}O₂ films and their photocatalytic activities under visible light irradiation*, Materials Science and Engineering B **108**(3), 2004, pp. 187–193.
- [11] KLOSEK S., RAFTERY D., *Visible light driven V-doped TiO₂ photocatalyst and its photooxidation of ethanol*, Journal of Physical Chemistry B **105**(14), 2001, pp. 2815–2819.
- [12] SERPONE N., LAWLESS D., DISDIER J., HERRMANN J.-M., *Spectroscopic, photoconductivity, and photocatalytic studies of TiO₂ colloids: naked and with the lattice doped with Cr³⁺, Fe³⁺, and V⁵⁺ cations*, Langmuir **10**(3), 1994, pp. 643–652.
- [13] FUERTE A., HERNÁNDEZ-ALONSO M.D., MAIRA A.J., MARTÍNEZ-ARIAS A., FERNÁNDEZ-GARCÍA M., CONESA J.C., SORIA J., *Visible light-activated nanosized doped-TiO₂ photocatalysts*, Chemical Communications, No. 24, 2001, pp. 2718–2719.
- [14] SUE-MIN CHANG, WEI-SZU LIU, *Surface doping is more beneficial than bulk doping to the photocatalytic activity of vanadium-doped TiO₂*, Applied Catalysis B: Environmental **101**(3–4), 2011, pp. 333–342.
- [15] HONG LI, GAOLING ZHAO, GAORONG HAN, BIN SONG, *Hydrophilicity and photocatalysis of Ti_{1-x}V_xO₂ films prepared by sol-gel method*, Surface and Coatings Technology **201**(18), 2007, pp. 7615–7618.
- [16] WANG Y., DOREN D.J., *Electronic structures of V-doped anatase TiO₂*, Solid State Communications **136**(3), 2005, pp. 142–146.
- [17] PROCIOW E.L., DOMARADZKI J., SIERADZKA K., KACZMAREK D., MAZUR M., *Structural, electrical and surface static charge investigation of TiO₂ thin films doped with different amount of vanadium*, Proceedings of 32th International Spring Seminar on Electronics Technology, 2009, Brno, Czech Republic, pp. 1–5.
- [18] SIERADZKA K., PROCIOW E.L., DOMARADZKI J., MAZUR M., KACZMAREK D., *Electrical investigation of transparent thin films based on TiO₂ doped with palladium and vanadium*, 2009 International Students and Young Scientists Workshop “Photonics and Microsystems”, Wernigerode, Germany (IEEE, Piscataway, 2009), pp. 72–76.
- [19] PROCIOW E.L., DOMARADZKI J., KACZMAREK D., BERLICKI T., Polish patent No. P382163, 2007.

- [20] DOMARADZKI J., PROCIOW E.L., KACZMAREK D., BERLICKI T., PODHORODECKI A., KUDRAWIEC R., MISIEWICZ J., *X-ray, optical and electrical characterization of doped nanocrystalline titanium oxide thin films*, *Materials Science and Engineering B* **109**(1–3), 2004, pp. 249–251.
- [21] ASTM Powder Diffraction Data Cards, International Centre for Diffraction Data, New York, 1983, Card 9-387.
- [22] BABELON P., DEQUIEDT A.S., MOSTÉFA-SBA H., BOURGEOIS S., SIBILLOT P., SACIOTTI M., *SEM and XPS studies of titanium dioxide thin films grown by MOCVD*, *Thin Solid Films* **322**(1–2), 1998, pp. 63–67.
- [23] CARRAWAY E.R., HOFFMAN A.J., HOFFMANN M.R., *Photocatalytic oxidation of organic acids on quantum-sized semiconductor colloids*, *Environmental Science and Technology* **28**(5), 1994, pp. 786–793.
- [24] SEONG-IL YOON, IN-GYUNG JUNG, MISOOK KANG, *Characterization of metal (Ba, Al, Si, V and W)-incorporated TiO₂ and toluene photodecomposition in the presence of H₂O*, *Korean Journal of Chemical Engineering* **24**(6), 2007, pp. 965–974.
- [25] SIERADZKA K., KACZMAREK D., DOMARADZKI J., PROCIOW E., MAZUR M., GÓRNICKA B., *Optical and electric al properties of nanocrystalline TiO₂:Pd semiconducting oxides*, *Central European Journal of Physics* **9**(2), 2011, pp. 313–318.
- [26] EUFINGER K., POELMAN D., POELMAN H., DE GRYSSE R., MARIN G.B., *Photocatalytic activity of dc magnetron sputter deposited amorphous TiO₂ thin films*, *Applied Surface Science* **254**(1), 2007, pp. 148–152.

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