# Correlation between Charge Transport and Photoelectrochemical Performance of TiO₂ Thin Films

K. Kulinowski[a], J. Leszczyński[b], M. Wołoszyn[a], B.J. Spisak[a], M. Radecka[b,*] and K. Zakrzewska[c]

[a]AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, al. A. Mickiewicza 30, 30-059 Kraków, Poland

[b]AGH University of Science and Technology, Faculty of Materials Science and Ceramics, al. A. Mickiewicza 30, 30-059 Kraków, Poland

[c]AGH University of Science and Technology, Faculty of Computer Science, Electronics and Telecommunication, al. A. Mickiewicza 30, 30-059 Kraków, Poland

Fast charge transport plays a decisive role in the subsequent performance of photoelectrochemical systems based on titanium dioxide photoanodes. This report concentrates on measurements of temperature dependence of the electrical resistivity of TiO₂, which are performed over the range extending from 15 K to 300 K in the current-in-plane geometry. Performed measurements prove that the transport properties of the considered system depend on stoichiometry of the samples.

## 1. Introduction

Importance of titanium dioxide in photocatalysis has been fully recognized since the first report concerning the photoelectrochemical solar cell published by Fujishima and Honda [1]. Photoelectrolysis of water — its decomposition into hydrogen and oxygen due to the absorption of sunlight by photoactive material — is considered as the most important non-conventional energy source of the future. This process is conducted in a photoelectrochemical cell (PEC), composed of aqueous electrolyte and two electrodes of which at least one should be formed from a semiconducting material — typically the anode. Titanium dioxide TiO₂ is one of the most suitable candidates for the photoanode material in PEC. Several strategies that could provide higher sunlight conversion efficiency and improve the photoresponse of TiO₂ have been proposed [2–4]. Four generations of TiO₂ photoanodes based on the modification of electronic structure are presented in the literature [4]. In this communication material properties other than band gap engineering are taken into consideration. The departure from stoichiometry in $TiO_{2-x}$ can be responsible for modification of band gap as well as for the additional states inside the forbidden gap of TiO₂ [4, 5]. Electrical conductivity of TiO₂ depends on the temperature range. At high temperatures (above room temperature) conduction mechanism can be explained by thermally activated processes [6, 7] with high activation energy (0.2–1.5 eV). At temperatures below 300 K the charge transport in TiO₂

is described by the hopping conduction [8–11]. From the electrical point of view, stoichiometric titanium dioxide is an insulator. Both the nonstoichiometry and the related point defect structure can be responsible for the electrical and photoelectrical properties of undoped titanium dioxide [5–7].

The purpose of this work is to study the correlation between charge transport and photoelectrochemical performance of TiO₂ thin films. In the previous work [12] the contributions of the concentration of charge carriers and mobility to the improved photoelectrochemical properties of the PEC were determined. The correlation between nonstoichiometry and thickness of TiO₂ thin films photoanodes was presented as well. Here, we have extended our investigations to the influence of deviation from stoichiometry on the temperature dependence of the electrical resistivity.

## 2. Experimental

Thin films of TiO₂ were deposited by means of the dc-pulsed reactive sputtering under optically controlled technological conditions. Especially $I/I_0$, which represents the technological parameter related to Ar emission line intensity at $\lambda = 500$ nm, was regarded as effective means of the controlling film stoichiometry. The ratio $I/I_0$ corresponds to the deviation from stoichiometry: higher $I/I_0$ indicates more oxygen-deficient compositions. The calibration of Ti/O atomic ratio vs. $I/I_0$ was performed in the previous paper [13]. The indium tin oxide (ITO) and amorphous silica were used as the substrates. The substrate temperature was 250 °C. Thickness of the deposited films varied from $d = 47$ nm to $d = 85$ nm. Measurements of the resistivity were performed over wide range of temperatures extending from

---

*corresponding author; e-mail: radecka@agh.edu.pl

15 to 300 K in the current-in-plane (CIP) geometry. They were carried out with a Keithley 6517A electrometer, through alternate cooling–heating–cooling of the sample procedure in cryostat. Two gold point electrodes separated by a distance of 10 mm were applied. Current–voltage characteristics for photoanodes in the dark and under illumination were recorded in PEC. The sputtering conditions and experimental details of photoelectrochemical measurements are described in details in [12]. Microstructure of the films was investigated by means of scanning electron microscope, SEM Nova NanoSem 200 equipped with an energy dispersive X-ray spectroscope. The Raman spectra were studied with Witec Alpha 300 M+ spectrometer. The above mentioned experimental methods allowed us to determine the parameters of titanium dioxide samples collected in Table I.

TABLE I

Basic parameters of $TiO_{2-x}$ thin films: $d$ — thin films thickness, $\sigma$ — electrical conductivity at room temperature (RT), and $I_{ph}$ — photocurrent at 0.5 V.

| $I/I_0$ | $d$ [nm] | $\sigma$ at RT $[(\Omega\ cm)^{-1}]$ | $I_{ph}$ at 0.5 V $[\mu A]$ |
|---|---|---|---|
| 0.16 | 50 | 0.132 | 287 |
| 0.20 | 47 | 0.201 | 184 |
| 0.30 | 85 | 0.472 | 160 |

## 3. Results

Figure 1 presents an example of SEM images and Raman spectra for $TiO_2$ thin films obtained at $I/I_0 = 0.20$. It is clearly demonstrated that thin films reproduce the morphology of the substrate, which consists of grains with diameter of about 20–30 nm. The Raman spectra with six bands at 144 cm$^{-1}$ ($E_{g(1)}$), 197 cm$^{-1}$ ($E_{g(2)}$), 399 cm$^{-1}$ ($B_{1g(1)}$), 513 cm$^{-1}$ ($A_{1g}$), 519 cm$^{-1}$ ($B_{1g(2)}$), and 639 cm$^{-1}$ ($E_{g(3)}$) can be assigned to $TiO_2$ anatase tetragonal structure [14]. Unfortunately, only one distinct band of $E_{g(1)}$ is visible, which is related to the significant contribution of amorphous phase.

Examples of the current–voltage characteristics measured in the photoelectrochemical cell are presented in Fig. 2. The flat band potential $V_{FB}$ was determined as the potential of the photocurrent's onset. $V_{FB}$ is negative and close to $-0.51$ V. The results show that the PEC with photoanodes based on $TiO_2$ thin films fulfils the requirements of a well-performing cell. This is evidenced by the positive anodic photocurrent with much higher values than the dark current within the same voltage range and the negative flat band potential. In the inset, the photocurrent values at $V_B = 0.5$ V vs. electrical conductivity of $TiO_2$ thin films are presented. It was found that the photocurrent of photoanodes is highly sensitive to electrical properties of the $TiO_{2-x}$ thin films.
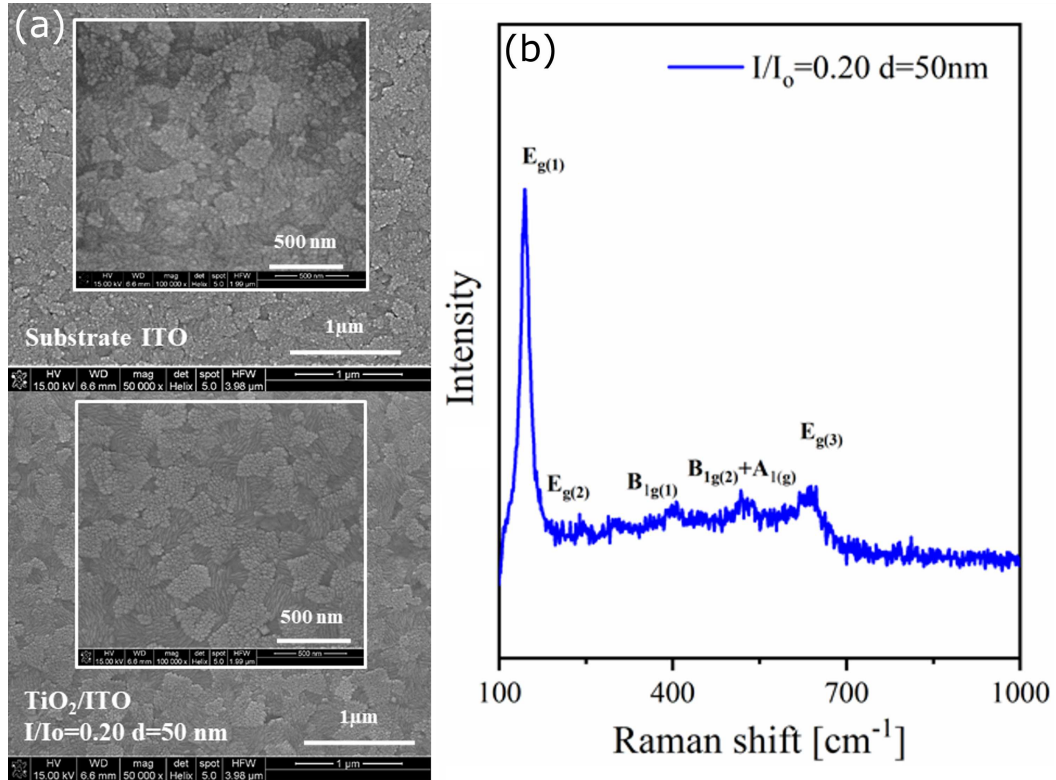


Fig. 1. (a) SEM top surface images of substrate (ITO) and $TiO_2$, (b) the Raman spectra for $TiO_2$. Thin films were obtained at $I/I_0 = 0.20$, $d = 50$ nm.
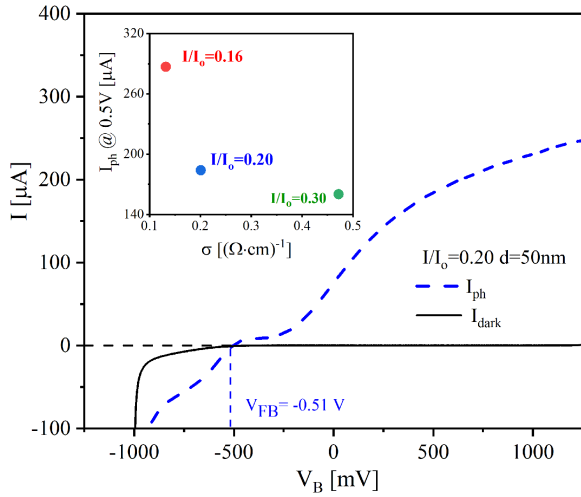
Fig. 2. Current–voltage dependence for photoanodes based on the thin films obtained at $I/I_0 = 0.20$. The inset shows the photocurrent $I_{ph}$ values at $V_B = 0.5$ V vs. electrical conductivity of TiO₂ thin films.
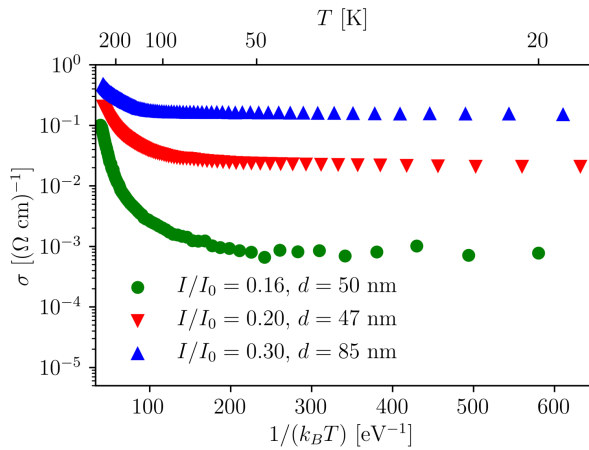


Fig. 3. Experimentally determined temperature dependence of the electrical conductivity of TiO₂ thin films.

Figure 3 illustrates the experimental results of the electrical conductivity as a function of temperature for thin films obtained at different $I/I_0$. As can be seen changes in the conditions of the film growth from oxidizing ($I/I_0 = 0.16$) through slightly under-oxidized ($I/I_0 = 0.20$) up to slightly reduced ($I/I_0 = 0.30$) results in the conductivity increase. These changes are the greatest in the low temperature range as opposed to room temperature.

In all cases a similar temperature dependence of conductivity is observed. Analysis of these plots of conductivity on a logarithmic scale versus reverse temperature show that no single conduction mechanism can fit the entire $\ln(\sigma)$ vs. $1/T$ curve. The data reveal a continuously varying slope in $\sigma$, followed by saturation at low temperatues. With the decrease in the $I/I_0$, the width of this temperature range narrows.
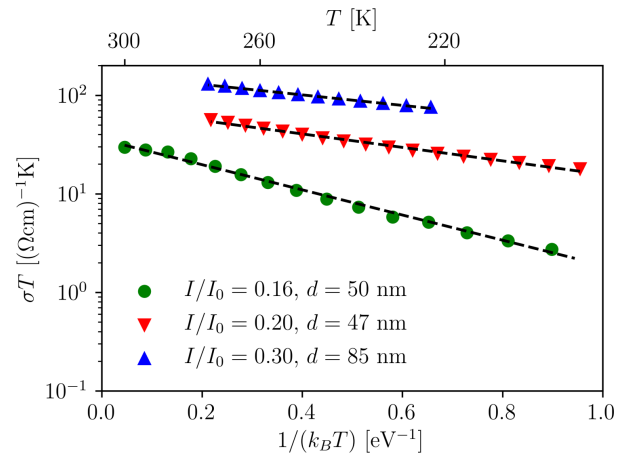


Fig. 4. Fit of $\ln(\sigma T)$ vs. $1/T$ to the experimental dependence from Fig. 3 within limited temperatures range.

In semiconductors with narrow conduction band which is typical for transition metal oxides including TiO₂, and relatively strong coupling between an electron and optical phonon, small polarons are formed. In this case, electrons are self-trapped at given lattice sites and can move only to a neighbouring unoccupied sites by an activated hopping process. The conduction of TiO₂ can be explained by the hopping mechanism [8–11]. For the considered system (titanium dioxide) the electron hopping is described by a polaron model whereby a negative polaron is localized at $Ti^{3+}$ site and electron jumps to an adjacent unoccupied $Ti^{4+}$ site. In this case the small-polaron hopping (SPH) model can be used at temperatures higher than half of the Debye temperature $\Theta_D$ [8]. In this model, there are two possible regimes: adiabatic and nonadiabatic [8]. In the adiabatic regime, polarons are thermally activated and higher probability of hopping to a neighbouring unoccupied site is observed. In turn, probability of carrier hopping is small for the non-adiabatic regime. Temperature dependences of conductivity for titanium dioxide thin films are presented in Fig. 3. Within these data we consider the high temperature range (see Fig. 4) in which the conductivities of the samples are consistent with the SPH model in the adiabatic regime, i.e., $\sigma$ can be expressed by the formula

$$\sigma = \frac{\sigma_0}{T} \exp\left(-\frac{W}{k_B T}\right), \qquad (1)$$

where $W$ is the activation energy, $k_B$ is the Boltzmann constant, $T$ is temperature, and $\sigma_0$ is the pre-exponential factor. From these data, the value of $\Theta_D/2$ was determined from the dependence $\ln(\sigma T)$ versus $1/T$ using the standard procedure [8]. The calculated values of the Debye temperature $\Theta_D$, the pre-exponential factor $\sigma_0$, the activation energy $W$, and the Pearson coefficient $r$ are collected in Table II.

In the general case, the activation energy $W$ may be treated as the sum of the enthalpy of charge carriers formation and activation energy of mobility. However, for a range of temperature below 300 K, it can be

TABLE II

Parameters calculated from the SPH model of conductance.

| $I/I_0$ | $d$ [nm] | $\Theta_\mathrm{D}$ [K] | $\sigma_0$ [K/($\Omega$ cm)] | $W$ [meV] | $r$ |
|---------|----------|-------------------------|------------------------------|-----------|------|
| 0.16 | 50 | 384 | $5.88\times10^3$ | 135.3 | -0.997 |
| 0.20 | 47 | 396 | $8.89\times10^2$ | 66.4 | -0.995 |
| 0.30 | 85 | 460 | $8.98\times10^2$ | 47.1 | -0.995 |

assumed that the activation energy of conductivity depends only on the mobility of charges carriers [7]. On the other hand, mobility of electronic charges in $TiO_2$ shows temperature-activated character. The value of the activation energy $W$ decreased from 135.3 meV to 47.1 meV with increase of nonstoichiometry. This effect is due to increase of donor concentration related to departure from stoichiometry.

## 4. Conclusions

In this work, the influence of nonstoichiometry on electrical and photoelectrochemical properties of $TiO_2$ thin films was studied. It was found that electrical conductivity of $TiO_2$ is correlated with increasing nonstoichiometry which results in changes of charge carrier concentration. The photocurrent decrease with departure from stoichiometry was attributed to increased recombination processes. The activation energy of conductivity determined from small-polaron hopping model decreases with an increased departure from stoichiometry.

## Acknowledgments

## References

[1] A. Fujishima, K. Honda, *Nature* **238**, 37 (1972).
[2] Y. Ma, X. Wang, Y. Jia, X. Chen, H. Han, C. Li, *Chem. Rev.* **114**, 9987 (2014).
[3] X. Chen, S.S. Mao, *Chem. Rev.* **107**, 2891 (2007).
[4] M. Radecka, A. Kusior, A. Trenczek-Zajac, K. Zakrzewska, *Adv. Inorg. Chem.* **72**, 145 (2018).
[5] B. Wang, S. Shen, S.S. Mao, *J. Materiomics* **3**, 96 (2017).
[6] R.G. Breckenridge, W.R. Hosler, *Phys. Rev.* **91**, 793 (1953).
[7] F.A. Grant, *Rev. Mod. Phys.* **32**, 646 (1959).
[8] A. Yildiz, F. Iacomi, D. Mardare, *J. Appl. Phys.* **108**, 083701 (2010).
[9] M. Kneiss, M. Jenderka, K. Brachwitz, M. Lorenz, M. Grundmann, *Appl. Phys. Lett.* **105**, 062103 (2014).
[10] D. Mardare, G.I. Rusu, *Mater. Sci. Eng. B* **75**, 68 (2000).
[11] S.P. Heluani, D. Comedi, M. Villafuerte, G. Juárez, *Physica B* **398**, 305 (2007).
[12] M. Radecka, A. Brudnik, K. Kulinowski, A. Kot, J. Leszczyński, J. Kanak, K. Zakrzewska, *J. Electron. Mater.* **48**, 5481 (2019).
[13] K. Zakrzewska, *Adv. Mater. Sci. Eng.* **2012**, 1 (2012).
[14] T. Ohsaka, F. Izumi, Y. Fujiki, *J. Raman Spectrosc.* **7**, 321 (1978).