BULLETIN OF THE POLISH ACADEMY OF SCIENCES
TECHNICAL SCIENCES, Vol. 62, No. 3, 2014
DOI: 10.2478/bpasts-2014-0063

Optical and electrical properties of (Ti-V)O_x thin film as n-type Transparent Oxide Semiconductor

M. MAZUR*, J. DOMARADZKI, and D. WOJCIESZAK

Faculty of Microsystem Electronics and Photonics, Wroclaw University of Technology,
11/17 Janiszewskiego St., 50-372 Wroclaw, Poland

Abstract. In this paper, the influence of vanadium doping on optical and electrical properties of titanium dioxide thin films has been discussed. The (Ti-V)O_x thin films was deposited on silicon and Corning glass substrates using high energy reactive magnetron sputtering process. Measurements performed with the aid of x-ray diffraction revealed, that deposited thin film was composed of nanocrystalline mixture of TiO_2-anatase, V_2O_3 and β-V_2O_5 phases. The amount of vanadium in the thin film, estimated on the basis of energy dispersive spectroscopy measurement, was equal to 3 at. %. Optical properties were evaluated based on transmission and reflection measurements. (Ti-V)O_x thin film was well transparent and the absorption edge was shifted by only 11 nm towards longer wavelengths in comparison to undoped TiO_2. Electrical measurements revealed, that investigated thin film was transparent oxide semiconductors with n-type electrical conduction and resistivity of about $2.7 \cdot 10^5$ Ωcm at room temperature. Additionally, measured I-V characteristics of TOS-Si heterostructure were nonlinear and asymmetrical.

Key words: Transparent Oxide Semiconductor, Transparent Electronics, (Ti-V)O_x thin film, magnetron sputtering, optical and electrical properties.

1. Introduction

The significant alternative for classical semiconductor materials are selected thin oxide films with high transparency for visible light and ability to conduct electrical charge carriers at room temperature [1]. Therefore, in recent years increased interest in novel oxide materials with given and strictly specified properties has been observed [2–5]. Such materials form an entirely new field of science, called Transparent Electronics. According to the resistance value, thin oxide films prepared for the purpose of Transparent Electronics can be divided into two separate groups: Transparent Conducting Oxides (TCO) with resistivity less than 10^{-3} Ωcm and Transparent Oxide Semiconductors (TOS) with resistivity in the range from 10^{-3} Ωcm to 10^8 Ωcm. Increased concern of TCO and TOS materials is also caused by their additional properties, which may be e.g. hydrophobicity, photocatalytic or antireflective properties [2–5].

In the current state of the art there are some scientific publications devoted to preparation and characterization of TOS materials, which concern mainly ZnO, ITO and SnO_2 oxides [6–8]. There are also some reports about manufacturing of TOS thin films based on titanium dioxide [9–11]. Publications, which concern the fabrication and the possibility of application of TOS-Si heterostructures have begun to appear in the recent years and have been focused only on ZnO, Cu_2O and In_2O_3 thin films [12, 13]. Combining of specific properties of thin oxide films with conventional silicon microelectronics is still a huge challenge.

However, up to now there are only few reports about the preparation of TOS-Si active heterostructures based on TiO_2 thin films [9, 14]. Unmodified TiO_2 has limited possibility of use in some fields of optoelectronics due to its low carriers mobility (< 10 cm^2/Vs), wide band gap (> 3 eV) and high electrical resistivity at room temperature ($\sim 10^{12}$ Ωcm). Incorporation of suitable dopants into TiO_2 matrix could increase its conductivity, yet it cause simultaneous and significant deterioration of its transparency in visible light range.

On the basis of experimental works conducted in the past [9, 11, 15], vanadium has been chosen as a dopant to modify electrical properties of TiO_2 for the purpose of deposition and characterization of TOS thin films. Vanadium can occur at various oxidation states, what enables on manufacturing of thin films with different crystallographic structure and properties [9, 16]. The basic advantage of doping TiO_2 with vanadium is significant resistivity decrease, while maintaining high transparency. However, addition of significant amount of vanadium to titanium dioxide can decrease the transparency level even to 60% and shift the absorption edge towards longer wavelength even of about 90 nm. Such a change of optical properties is undesirable in case of materials designed for the purpose of Transparent Electronics. Therefore, Authors decided to prepare thin film with less amount of vanadium to obtain the suitable compromise between high transparency and low resistivity.

In this work optical and electrical properties of (Ti-V)O_x transparent oxide semiconducting thin film have been discussed.

*e-mail: michal.mazur@pwr.wroc.pl

2. Experimental details

Thin film based on mixed titanium and vanadium oxides was deposited using high energy reactive magnetron sputtering process [17]. The target was composed of titanium and vanadium metallic wedges and sputtered in pure oxygen. Preparation of multicomponent thin films using such mosaic targets is easy and repeatable way, that allows on manufacturing thin films with a different composition. An additional heating of the target surface that originates from the reactive plasma and a specially designed pulse supplier were applied. As a result, sputtered species approaching the substrate had enhanced thermal energy for ordering themselves. Moreover, the increase in molecular energy during nucleation on the substrate resulted in an increased number of nucleation centers, which led to a significant reduction of grain sizes in the thin film. Parameters of magnetron sputtering process are summarized in Table 1. Thin film was deposited on p-type silicon substrates for the purpose of TOS-Si heterostructure preparation, while Corning 7059 glass was used to perform transmission and reflection measurements.

Table 1
Magnetron sputtering parameters during the deposition process of $(Ti\text{-}V)O_x$ thin film

Pressure [10^{-3} mbar]	Sputtering power [kW]	Deposition time [min]
3.53	0.91	60

The elemental composition and surface morphology of thin film were investigated with the aid of FESEM FEI Nova NanoSEM 230 scanning electron microscope.

To determine surface topography, the AFM measurements were performed by atomic force microscope UHV VT AFM/STM Omicron operating in ultra high vacuum conditions in contact mode.

The type of crystal structure and average crystallites size were determined based on the results of the x-ray diffraction (XRD) measurements using a Siemens D5005 powder diffractometer with Cu Kα ($\lambda = 0.154059$ nm) radiation.

Optical properties were evaluated on the basis of transmission and reflection measurements. The experimental system was based on Ocean Optics QE 65000 spectrophotometer and a coupled deuterium-halogen light source. Based on experimental results such parameters like transmission and reflection level, cut-off wavelength, absorption, real and imaginary parts of refractive index and values of optical band gap were evaluated. The analysis was performed using FTG FilmStar software.

Electrical properties of manufactured thin films were investigated with the aid of Keithley 4200 SCS semiconductor characterization system and Cascade Microtech M150 measurement station. Measurements of surface resistivity, thermal activation energy as well as Seebeck coefficient and I-V characteristics were performed.

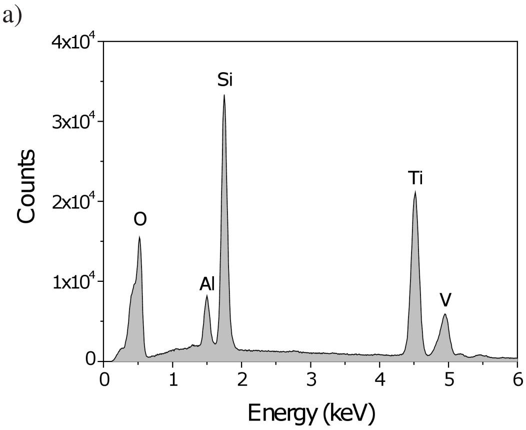
3. Results and discussion

The amount of vanadium dopant in the deposited thin film was analyzed using energy dispersive spectrometer and the estimated concentration was equal to 3.0 at. % with respect to titanium and oxygen content. EDS spectrum and SEM image of $(Ti\text{-}V)O_x$ thin film are shown in Fig. 1. Thin film is crack free, exhibits good adherence to the substrate and the surface morphology is homogenous.

The surface properties were also investigated using atomic force microscopy and the results are shown in Fig. 2. The surface structure is homogenous and densely packed. At the surface of thin film grains, which might be composed of several smaller crystallites, are visible.

The height distribution of the $(Ti\text{-}V)O_x$ thin film grains is shown in Fig. 3a. The height distribution was found to be symmetric, what testifies about homogenous distribution of grains in deposited thin film. On the basis of this distribution the RMS (Root Mean Square) roughness was evaluated and it was equal to 1.7 nm, while the average roughness was equal to 1.4 nm. The cross-section topography of the surface is shown in Fig. 3b. Abbott-Firestone curve, also called as the bearing plot, which is the percentage of the data points at, or above a given depth, has been determined. In case of investigated thin film it is the cumulative probability density function of the surface profile's height and the plot for $(Ti\text{-}V)O_x$ thin films is presented in Fig. 3c.

a)



b)

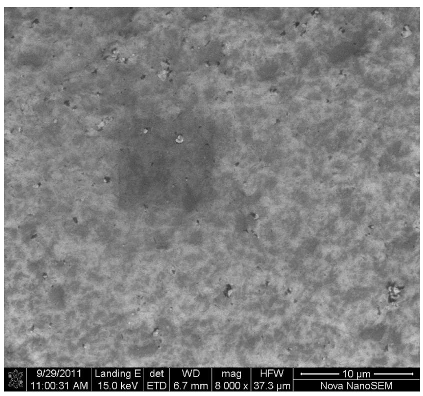


Fig. 1. Images of: a) EDS spectrum and b) surface of $(Ti\text{-}V)O_x$ thin film performed by SEM measurements

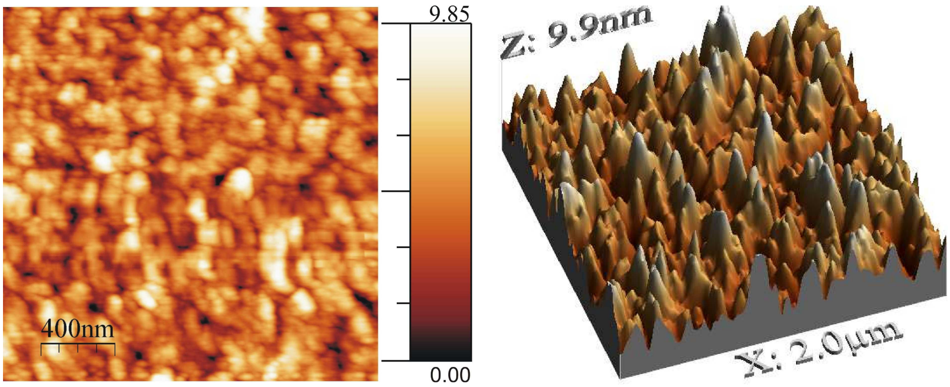


Fig. 2. AFM images of the surface topography of (Ti-V)O_x thin film

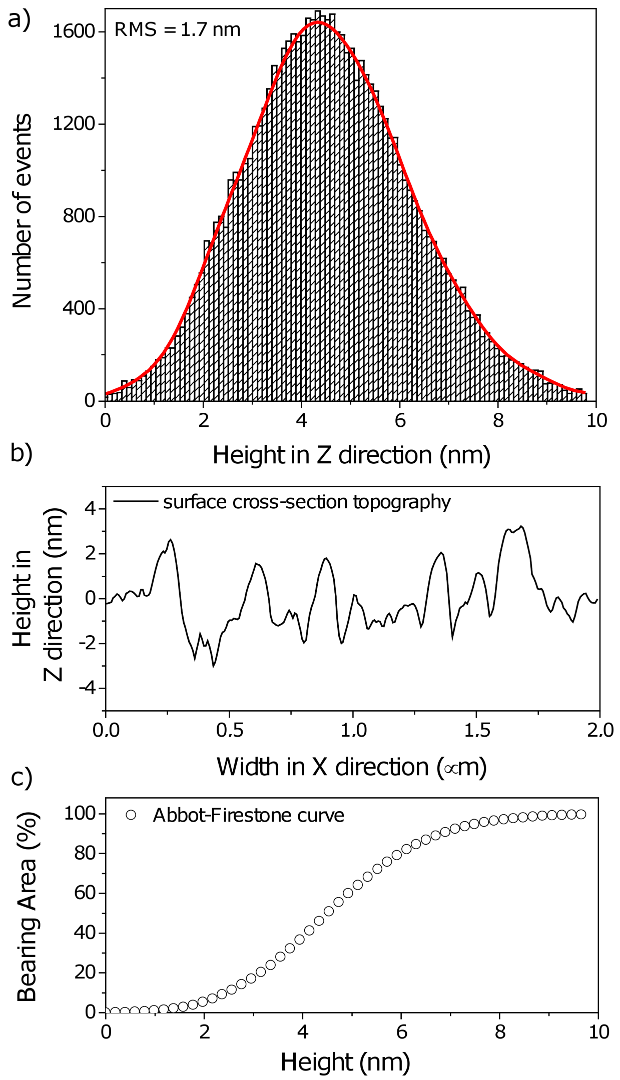


Fig. 3. Analysis results of AFM investigations: a) height distribution of grains size in Z direction, b) surface cross-section topography and c) Abbott-Firestone curve of (Ti-V)O_x thin film

XRD results (Table 2) showed, that deposited thin film was nanocrystalline and phases of TiO_2-anatase, V_2O_3 and β-V_2O_5 were identified by comparison the angles of particular reflections with standard Powder Diffraction Files [18–20].

Table 2
Structural properties of (Ti-V)O_x thin film based on XRD results [12]

Structure phase	Crystallite size (nm)	PDF Card
TiO_2-anatase	5.7	No 21-1272 [15]
V_2O_3	8.1	No 45-1074 [16]
$\beta-V_2O_5$	8.8	No 39-0774 [17]

Transmission and reflection spectra of (Ti-V)O_x thin film for random polarization are presented in Fig. 4. Deposited thin film is transparent in the visible and also in near infrared spectral range. The average transmission is equal to ca. 75%, what is almost as high as in case of undoped TiO_2 [9, 21]. However, the cut off wavelength is shifted from ca. 345 nm to 356 nm for TiO_2 and (Ti-V)O_x thin films, respectively. Visible maxima and minima are the result of interference effect occurring between waves transmitted and reflected from interfaces at the border of substrate – thin film and thin film – surrounding medium.

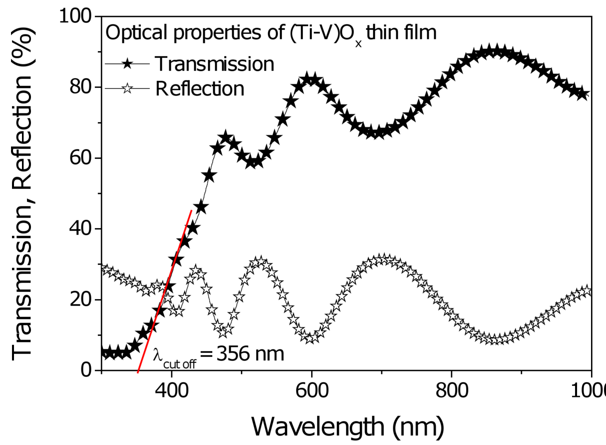


Fig. 4. Transmission and reflection spectra of (Ti-V)O_x thin film deposited on Corning glass substrate

Based on transmission spectrum presented in Fig. 4, refractive index and extinction coefficient were calculated using the FTG FilmStar software. The Generalized Cauchy model (for the thin films with extinction coefficients $k > 0$) was applied for the calculation of theoretical curves, which fits to experimental results of transmission. Correlation of transmission spectra of (Ti-V)O_x thin film determined experimentally and by reverse engineering method is presented in Fig. 5. Comparison of transmission spectra determined experimentally and theoretically by reverse engineering method is presented in Fig. 5. The mean squared error of the theoretical fit to the experimental points was equal to ca. 0.75% in the spectral range from 390 nm up to 1000 nm. The thickness of the film calculated from the model was 395 nm.

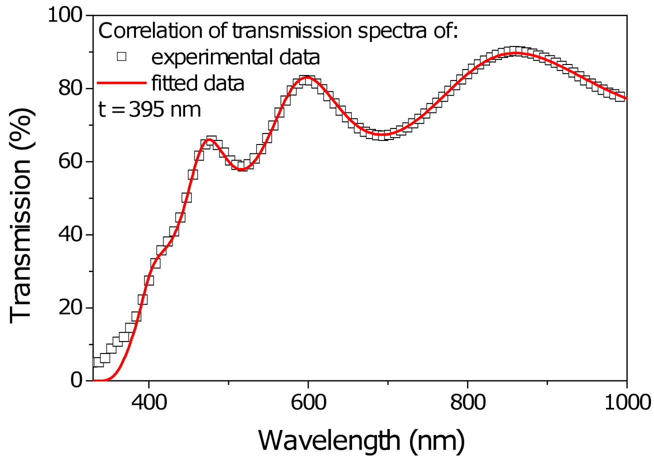


Fig. 5. Correlation of transmission spectra of (Ti-V)Ox thin film determined experimentally and by reverse engineering method. Designation: t – thickness of the thin film

Dispersion characteristics of refractive index have been calculated and presented in Fig. 6. Real and imaginary part of refractive index were calculated according to the following equations based on Generalized Cauchy model:

$$n = A + B \cdot \lambda^D + C \cdot \lambda^E, \tag{1}$$

$$k = \exp(F + G \cdot \lambda^H), \tag{2}$$

where $A \div H$ – parameters.

The value of refractive index was equal to $n = 2.29$ at $\lambda = 550$ nm (Fig. 3a), while the extinction coefficient $k = 1.8 \cdot 10^{-2}$ at $\lambda = 550$ nm (Fig. 3b). The low value of imaginary part of refractive index indicates on the low light absorption in investigated thin film.

In Fig. 7 absorption spectrum for (Ti-V)O_x thin film has been presented. Absorption edge for (Ti-V)O_x sample is shifted towards longer wavelengths as compared to TiO_2 [21]. In such case, compounds of titanium and vanadium oxides can absorb light in UV and in a part of visible light. Thanks to that these thin films possess better photocatalytic activity than TiO_2, what was found in previous works [21].

Based on transmission and absorption investigations the width of optical energy gap (E_g^{opt}) has been determined. Optical band gap was calculated using the Tauc equation [22]:

$$\alpha hv = A(hv - E_g)^m, \tag{3}$$

where A – constant, hv – the photon energy, α – absorption coefficient.

a)

b)

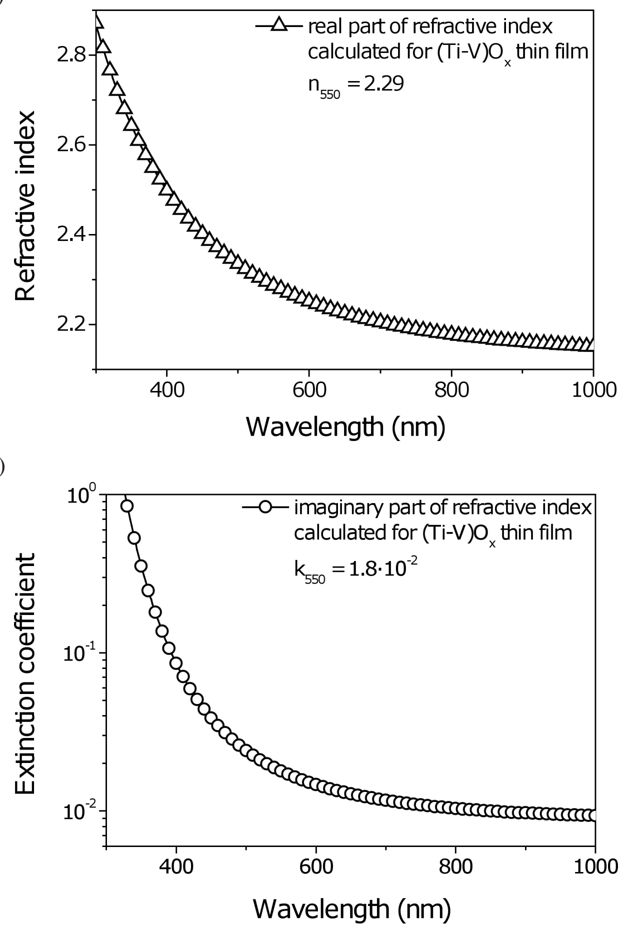


Fig. 6. Real (a) and imaginary (b) parts of refractive index calculated for (Ti-V)O_x thin film

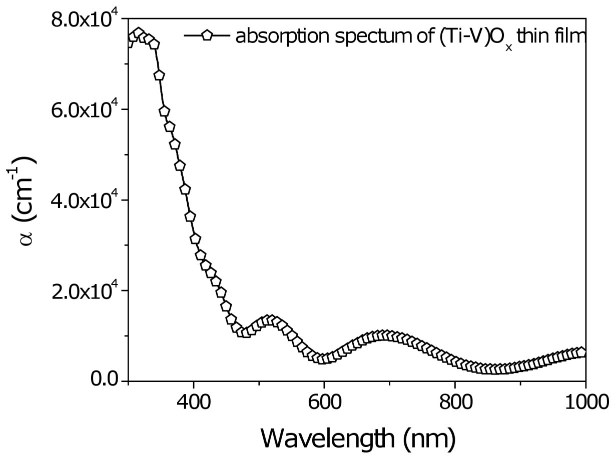


Fig. 7. Absorption spectrum of (Ti-V)O_x thin film

The value of m exponent can be equal to 2 or 1/2 for direct or indirect allowed transitions, respectively. The calculated Tauc plots for both types of transitions are shown in Fig. 8. Based on these results it was determined, that the direct transitions are predominant. Optical band gap is equal to 3.31 eV, what is about 0.49 eV lower than in case of undoped titanium dioxide of anatase structure [23].

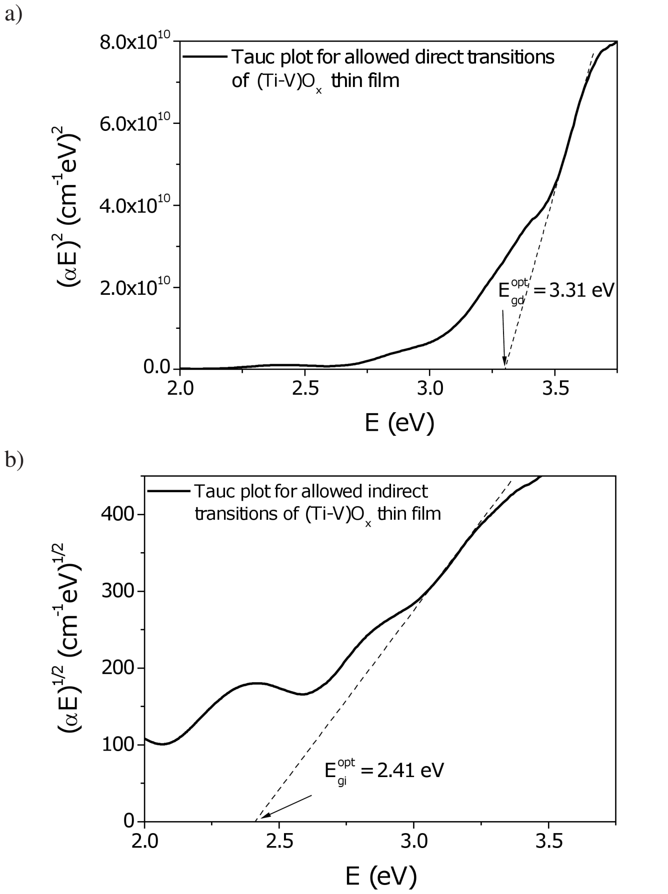


Fig. 8. Tauc plots for allowed: a) direct and b) indirect transitions of (Ti-V)O_x thin film. Designations: E_{gd}^{opt} – optical band gap for direct transitions, E_{gi}^{opt} – optical band gap for indirect transitions

The results of resistivity, thermal activation energy and Seebeck coefficients are shown in Table 3. Plot of the resistivity in the function of temperature has been shown in Fig. 9. It was found, that 3 at. % of vanadium had significant influence on the resistivity of thin film, which decreased of about six orders in comparison to undoped titanium dioxide. Value of resistivity at the room temperature places investigated thin film in the group of Transparent Oxide Semiconductors. On the basis of the slope of $\log(\rho) = f(1000/T)$, thermal activation energy was calculated using exponential Arrhenius formula [14]. The negative sign of Seebeck coefficient determined for (Ti-V)O_x thin film indicates on the electron type of electrical conduction.

Table 3
Electrical properties of (Ti-V)O_x thin film

Thin oxide film	ρ_{300K} [Ωcm]	W_ρ [eV]	S [μV/K]	Type of electrical conduction
(Ti-V)O_x	$2.7 \cdot 10^5$	0.31	-200	n

For the purpose of preparation of p-n junctions, materials of electron and hole types of electrical conduction are necessary. In this case, the n-type (Ti-V)O_x thin film was deposited on conventional p-type Si substrate. To confirm the formation of TOS-Si heterojunction, the I-V measurements were performed. Measured current-voltage characteristics in the lateral configuration are nonlinear, asymmetrical and presented in Fig. 10. The influence of light illumination on I-V characteristics of TOS-Si heterojunction based on (Ti-V)O_x thin film measured in the lateral configuration are presented in Fig. 11. In case of investigated TOS-Si heterojunction illuminated by the light, the significant increase of the current in reverse bias direction was observed, like in the case of conventional semiconductor.

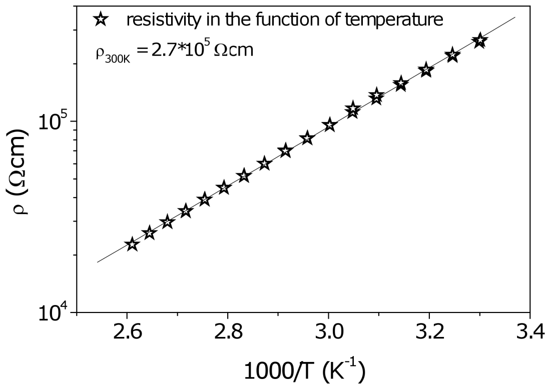


Fig. 9. Resistivity in the function of temperature of (Ti-V)O_x thin film deposited on Corning glass substrates

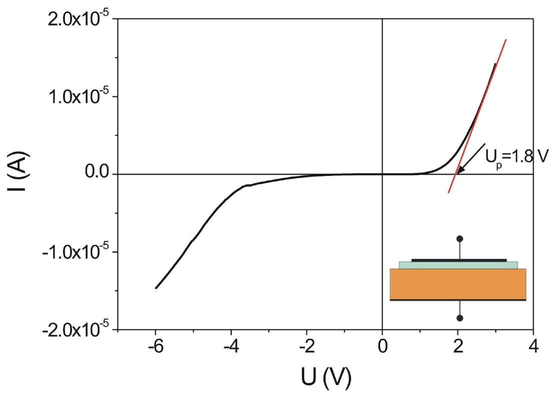


Fig. 10. I-V characteristics of TOS-Si heterojunction based on (Ti-V)O_x thin film measured in the lateral configuration. U_p – threshold voltage

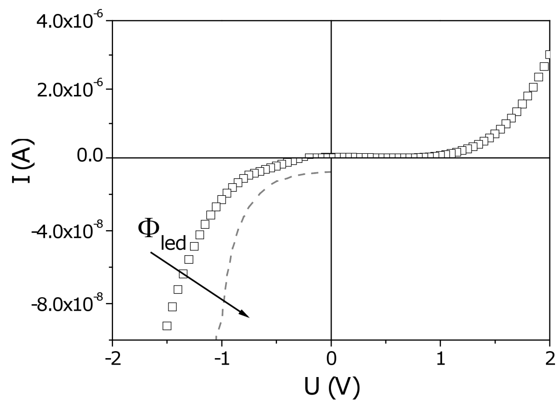


Fig. 11. Influence of light illumination on I-V characteristics of TOS-Si heterojunction based on (Ti-V)O_x thin film measured in the lateral configuration

4. Summary

The investigated thin film based on mixed titanium and vanadium oxides was deposited on p-type silicon and glass substrates using a high energy reactive magnetron sputtering process. The vanadium concentration in (Ti-V)O_x sample was equal to 3 at. %. The surface of the investigated thin film is homogenous and crack free. The RMS roughness is equal to 1.7 nm, while the average roughness is equal to 1.4 nm. XRD measurements revealed, that a deposited thin film was nanocrystalline with crystallites size smaller than 9 nm and TiO_2-anatase, V_2O_3 and β-V_2O_5 phases were identified.

The prepared thin oxide film is well transparent in the visible spectral range. The average transmission of (Ti-V)O_x thin film is almost as high as in a case of an undoped TiO_2, however the cut-off wavelength as well as absorption edge is shifted towards longer wavelengths. The value of a real part of refractive index is equal to $n = 2.29$ at $\lambda = 550$ nm and an extinction coefficient is low, which makes the investigated thin film suitable as, e.g. antireflective coatings for silicon solar cells. The direct transitions are predominant in the case of investigated thin films and the optical band gap is 3.31 eV, what is lower than in the case of undoped TiO_2 of an anatase structure. Therefore, such a change can be related to the doping thin films with vanadium.

Addition of vanadium dopant into TiO_2 matrix has slightly changed its transparency, however it had significant influence on the resistivity level, which has decreased of about six orders to ca. $2.7 \cdot 10^5$ Ωcm. Electrical measurements revealed also, that (Ti-V)O_x thin films are n-type Transparent Oxide Semiconductors. Measured I-V characteristics in the lateral configuration are nonlinear and asymmetrical, what indicates on forming of TOS-Si heterostructure.

Acknowledgements. The authors would like to thank Prof. D. Kaczmarek and PhD K. Sieradzka from the Wroclaw University of Technology for a valuable discussion and helpful comments on investigation results.

This work was co-financed from the sources given by the NCN as research projects under the number N N515 4970 40, DEC-2013/09/B/ST7/01592 and from the project B30067.

REFERENCES

[1] A. Facchetti and T.J. Marks, *Transparent Electronics – From Synthesis to Applications*, John Wiley & Sons Ltd., London, 2010.

[2] I.P. Parkin and R.G. Palgrave, "Self-cleaning coatings", *J. Mater. Chem.* 15, 1689–1695 (2005).

[3] S-Y. Lien, D.S. Wuu, W.C. Yeh, and J.C. Liu, "Tri-layer antireflection coatings (SiO_2/SiO_2-TiO_2/TiO_2) for silicon solar cells using a sol-gel technique", *Sol. Ener. Mater. Solar Cells* 90, 2710–2719 (2006).

[4] J. Kowalski, H. Szymanowski, A. Sobczyk-Guzenda, and M. Gazicki-Lipman, "A stack multilayer high reflectance optical filter produced on poliester substrate with the PECVD technique", *Bull. Pol. Ac.: Tech.* 57 (2), 171–176 (2009).

[5] T. Pustelny, M. Procek, E. Maciak, A. Stolarczyk, S. Drewniak, M. Urbańczyk, M. Setkiewicz, K. Gut, and Z. Opilski, "Gas sensors based on nanostructures of semiconductors ZnO and TiO_2", *Bull. Pol. Ac.: Tech.* 60 (4), 853–859 (2012).

[6] E. Fortunato, P. Barquinha, A. Pimentel, A. Gonçalves, A. Marques, L. Pereira, and R. Martins, "Recent advances in ZnO transparent thin film transistors", *Thin Solid Films* 487, 205–211 (2005).

[7] Y. Hayashi, K. Kondo, K. Murai, T. Moriga, I. Nakabayashi, H. Fukumoto, and K. Tominaga, "ZnO-SnO_2 transparent conductive films deposited by opposed target sputtering system of ZnO and SnO_2 targets", *Vacuum* 74, 607–611 (2004).

[8] C.G. Granqvist and A. Hultaker, "Transparent and conducting ITO films: new developments and applications", *Thin Solid Film* 411, 1–5 (2002).

[9] K. Sieradzka, M. Mazur, D. Wojcieszak, J. Domaradzki, D. Kaczmarek, and E. Prociów, "P-type transparent Ti-V oxides semiconductor thin film as a prospective material for transparent electronics", *Thin Solid Films* 520, 3472–3476 (2012).

[10] E. Prociów, K. Sieradzka, J. Domaradzki, D. Kaczmarek, and M. Mazur, "Thin films based on nanocrystalline TiO_2 for transparent electronics", *Acta Phys. Pol.* A 116, S-72–S-74 (2009).

[11] K. Sieradzka, J. Domaradzki, E. Prociów, M. Mazur, and M. Łapiński, "Properties of nanocrystalline TiO_2:V thin films as a transparent semiconducting oxides", *Acta Phys. Pol.* A 116, S-33–S-35 (2009).

[12] M. Kumar, J.P. Kar, I.S. Kim, S.Y. Choi, and J.M. Myoung, "Growth of p-type ZnO thin film on n-type silicon substrate and its application as hybrid homojunction", *Curr. Appl. Phys.* 11, 65–69 (2011).

[13] T. Serin, S. Gurakar, N. Serin, N. Yildirim, and F.O. Kus, "Current flow mechanism in Cu_2O/p-Si heterojunction prepared by chemical method", *J. Phys. D: Appl. Phys*. 42, 1–5 (2009).

[14] K. Sieradzka, D. Kaczmarek, J. Morgiel, J. Domaradzki, E. Prociow, and B. Adamiak, "Structural properties of Ti-V oxide semiconductor thin films", *Cent. Eur. J. Phys*. 11 (2), 251–257 (2012).

[15] M. Mazur, K. Sieradzka, D. Kaczmarek, J. Domaradzki, D. Wojcieszak, P. Domanowski, and E. Prociów, "Investigation of physicochemical and tribological properties of transparent oxide semiconducting thin films based on Ti-V oxides", *Mater. Sci.-Poland* 31 (3), 434–445 (2013).

[16] S. Surnev, M.G. Ramsey, and F.P. Netzer, "Vanadium oxide surface studies", *Progr. Surf. Sci.* 73, 117–165 (2003).

[17] D. Kaczmarek, E. Prociow, J. Domaradzki, A. Borkowska, W. Mielcarek, and D. Wojcieszak, "Influence of substrate type and its placement on structural properties of TiO_2 thin films prepared by the high energy reactive magnetron sputtering method", *Mater. Sci.-Poland* 26 (1), 113–117 (2008).

[18] *Powder Diffraction Files,* No 21-1272, Philadelfia, 1967.

[19] *Powder Diffraction Files,* No 39-0774, Philadelfia, 1990.

[20] *Powder Diffraction Files*, No 45-1074, Philadelfia, 2000.

[21] J. Domaradzki, M. Mazur, K. Sieradzka, D. Wojcieszak, and B. Adamiak, "Photocatalytic properties of Ti-V oxides thin films", *Opt. Appl.* 43 (1), 153–162 (2013).

[22] J. Tauc, "Absorption edge and internal electric fields in amorphous semiconductors", *Mater. Res. Bull.* 5 (8), 721–729 (1970).

[23] Z. Wang, U. Helmersson, and P. Kall, "Optical properties of anatase TiO_2 thin films prepared by aqueous sol-gel process at low temperature", *Thin Solid Films* 405 (1–2), 50–54 (2002).