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Investigation of physicochemical and tribological properties of transparent oxide semiconducting thin films based on Ti–V oxides

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In this paper investigations of structural and optical properties of nanocrystalline Ti–V oxide thin films are described. The films were deposited onto Corning 7059 glass using a modified reactive magnetron sputtering method. Structural investigations of prepared Ti–V oxides with vanadium addition of 19 at. % revealed amorphous structure, while incorporation of 21 and 23 at. % of vanadium resulted in V_2O_5 formation with crystallites sizes of 12.7 and 32.4 nm, respectively. All prepared thin films belong to transparent oxide semiconductors due to their high transmission level of ca. 60 – 75 % in the visible light range, and resistivity in the range of $3.3 \cdot 10^2 - 1.4 \cdot 10^5$ Ωcm. Additionally, wettability and hardness tests were performed in order to evaluate the usefulness of the films for functional coatings.

Keywords: *Ti–V oxide thin films; transparent oxide semiconductors; magnetron sputtering; tribological properties*

1. Introduction

Nowadays, transparent oxide semiconductors (TOSs) are widely studied due to their potential application in transparent electronics [1]. Wide optical band gap and relatively high electrical conduction of such materials make possible fabrication of advanced integrated optoelectronics devices. One of the promising wide band gap material, among often studied [2, 3] ZnO, SnO_2 and ITO, is TiO_2 doped with various elements [4–6]. TiO_2 is transparent, chemically inert, thermally stable, corrosion resistant, non-toxic and relatively inexpensive [7]. Recently, many authors have reported that thin films based on TiO_2, due to exceptional properties and presence of catalytic, electrochromic and photochromic effects, are widely applied in e.g. high resistant optical coatings or gas-sensing devices. Some properties of TiO_2 thin films, like transmittance and reflectance, refractive index or cut-off wavelength, are dependent on their microstructure [8]. The structure of TiO_2 thin films also influences mechanical properties, such as hardness, Young's modulus or stress strain. Thus, for example, porous and columnar thin films of oxide materials have been proposed as antireflective, self-cleaning and similar coatings [9–11].

Suitable doping can significantly change certain properties of TiO_2. Incorporation of e.g. Nb improves thermal stability in case of gas sensors [6], while transition elements like Cr, Mo or W can be used as dopants to TiO_2 to receive gasochromic effect [12, 13]. Moreover, doping with rare earth elements like Eu, Nd, Tb makes TiO_2 thin films optically active and enables us to obtain photoluminescence effect or improved photocatalytic activity [14, 15]. Also various electrical properties can be obtained by doping with e.g. Hf (insulator) [16] or V and Pd (semiconductor) [5, 17]. However, it seems that vanadium is one of few dopants, which makes capable to lower the resistivity and simul-

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taneously keep the high transparency of TiO_2 thin films. The V-containing mixed oxide materials are often used in catalytic, as well as non-catalytic applications, especially in electronics, optics or optoelectronics [6, 18]. As it was previously reported by the authors and what is worth to emphasize, doping of titanium dioxide with a proper amount of the dopant can result in obtaining transparent materials with p- or n-type of electrical conduction [6, 14].

In the present state of the art there is a lack of such investigations as, e.g. nanoindentation or wettability of transparent oxide semiconducting thin films. Therefore, the aim of this study was a detailed characterization of mixed Ti–V oxide thin films prepared by magnetron sputtering method. The studies were focused on the physicochemical, electrical, optical parameters, which are important for optical coatings in selected applications, including protective and self-cleaning coatings. The optical transmission and reflection spectra, electrical resistivity, hardness and contact angle results were discussed and correlated with the structural properties and surface roughness.

2. Experiment

The thin films were prepared by high energy reactive magnetron sputtering (HE RMS) method [19] using Ti–V mosaic target with various numbers of vanadium wedges. The sputtering process was carried out at low pressure (0.1 Pa), in reactive atmosphere using high purity oxygen as a working gas. Also, the enhancement of the target temperature close to its melting point has been applied. To avoid target overheating, the power was applied in pulses by a magnetron power supply working in the unipolar mode with sinusoidal pulses of 165 kHz, and 1.6 kHz, grouped together. All modifications have been applied to obtain thin films with densely packed structure. Detailed description of the preparation method has already been described elsewhere [20]. The films were deposited onto Corning 7059 glass substrates. The atomic percent of the elements in the prepared thin films was determined using energy dispersive spectrometer (Noran Vantage).

Structural properties of Ti–V oxide thin films were characterized by X-ray Diffraction (XRD) using DRON-2 powder diffractometer with Fe-filtered Co Kα radiation. Crystallites sizes were calculated using Sherrer's formula [21]. Surface morphology of deposited samples was examined with an atomic force microscope UHV VT AFM/STM Omicron operating in contact mode.

Electrical properties of the prepared thin films were measured with the aid of Keithley 4200 SCS semiconductor characterization system and Cascade Microtech M150 measurement station. ERS SP172 temperature controller was used to measure d.c. electrical resistivity in the temperature range of 300 – 383 K.

Transmission characteristics of Ti–V oxide thin films doped with 19, 21 and 23 at. % of vanadium were measured with a Hitachi U-3501 spectrophotometer at a normal incidence of light to the sample surface. Optical properties of the thin films were further investigated using an Aquila NKD-8000 spectrophotometer equipped with Pro-Optix software. This apparatus is designed to measure transmittance and reflectance simultaneously and to analyse these data in order to determine the properties of a thin film such as refractive index and the thickness. The spectra were recorded at an angle of incidence of 30 degrees, for S and P polarisation. Fitting of experimental results for Ti–V oxides was made using Drude-Lorentz dispersion model with 5 oscillators and Powell's analysis. The calculations were performed using Pearson's test – χ^2 (Chi-square).

Hardness measurements were performed with Hysitron Triboscope nanoindenter equipped with a flat Berkovich tip. For each loading/unloading cycle, the applied load value was plotted with respect to the corresponding position of the indenter. The result in the form of load-displacement curve was then analysed to determine mechanical properties of the sample material such as e.g. hardness, Young's modulus, stress-strain studies, or fracture toughness. During the measurement the Berkovich tip makes an indent with a force, which is specially adjusted to the thickness of the film. Based on this investigation, hardness (H) and reduced elastic modulus (E_r) can be defined. Analyses of ex-

perimental results of tribological and AFM investigations were done with the aid of WSxM ver. 5.0 software.

Surface properties characterization was performed through wettability measurements. The contact angle (θ) can be used to relate the thermodynamic properties of thin film surface. Using Young's equation [22] we can characterize liquid-solid-vapour system as:

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl}, \qquad (1)$$

where γ_{lv}, γ_{sv} and γ_{sl} are the liquid-vapour, solid-vapour and solid-liquid interface energies of a solid, respectively. However, only the values of contact angle and the liquid-vapour energy γ_{lv} can be obtained by experimental method and the rest of the parameters should be estimated experimentally. In the microscopic approach, the total surface free energy of a measured sample is a sum of its dispersive and polar components.

Another way to characterize the wettability of different materials is a method proposed by Zisman [23, 24]. Using a series of homologous and nonpolar liquids with different surface tensions, a graph of $\cos\theta$ vs. γ should be determined. Critical surface tension equals the surface tension at which the plotted line intersects the point 1.0. It is often interpreted as the highest value of surface tension of a liquid, which will completely wet the solid surface. This approach is most appropriate for low energy surfaces, which are being wetted by nonpolar liquids.

The measurements of contact angle and surface free energy were carried out with a computer controlled Attension Theta Lite tensiometer. Liquids used for the contact angle determination were water, ethylene glycol and ethanol. The contact angle measurements were performed according to the sessile drop method [24]. The contact angle results were used to calculate critical surface tension and surface free energies of the Ti–V oxide thin films.

3. Results

XRD measurements results and AFM images of Ti–V oxide thin films with different amount of vanadium have been shown in Fig. 1. Structural investigation of Ti–V oxide thin films showed that the thin films were densely packed and their surface morphology was dependent on the amount of V incorporated into the thin films. Thin films with vanadium addition of 19 at. % were amorphous, while 21 and 23 at. % of vanadium resulted in crystallization of the V_2O_5 phase with the crystallites of 12.7 and 32.4 nm in average size, respectively. The grains visible in the images are much bigger than the calculated from XRD patterns, which indicates that they might be composed of several smaller crystallites. The surface roughness (RMS) was ca. 3.6, 25.3 and 14.4 nm for Ti–V oxide thin films with vanadium addition of 19, 21 and 23 at. %, respectively.

The results of resistivity measurements are shown in Fig. 2. It was observed, that with the increase of vanadium addition, the resistivity decreased from $1.4 \cdot 10^5$ to $2.1 \cdot 10^3$ and $3.3 \cdot 10^2$ Ωcm at room temperature. Additionally, based on the slope of $\log(\rho) = f(1000/T)$, thermal activation energies E_ρ were calculated using exponential Arrhenius formula [25] and their values were in the range of 0.25 – 0.35 eV. In case of investigated samples, the thermal activation energies have also decreased with a decrease in resistivity.

Transmittance spectra of Ti–V oxides for random polarization at normal incidence of light to the sample surface have been compared in Fig. 3. The prepared Ti–V oxide thin films are well transparent in visible and also in near infrared spectral ranges. However, as it can be seen from the characteristics, the increased amount of vanadium addition caused the decrease of average transmittance, which is equal to ca. 75 %, 70 % and 60 % for Ti–V oxides with V addition of 19, 21 and 23 at. %, respectively. Additionally, the red-shift of the cutoff wavelength is visible from ca. 380 nm to 410 nm and to 440 nm for Ti–V oxides with addition of 19, 21 and 23 at. % of V, respectively.

In Fig. 4, transmittance and reflectance spectra of investigated nanocrystalline Ti–V oxide thin films have been shown. Due to the measurements performed at the 30 degree angle of incident light there are visible differences between the spectra collected for S and P polarisation. Based on these
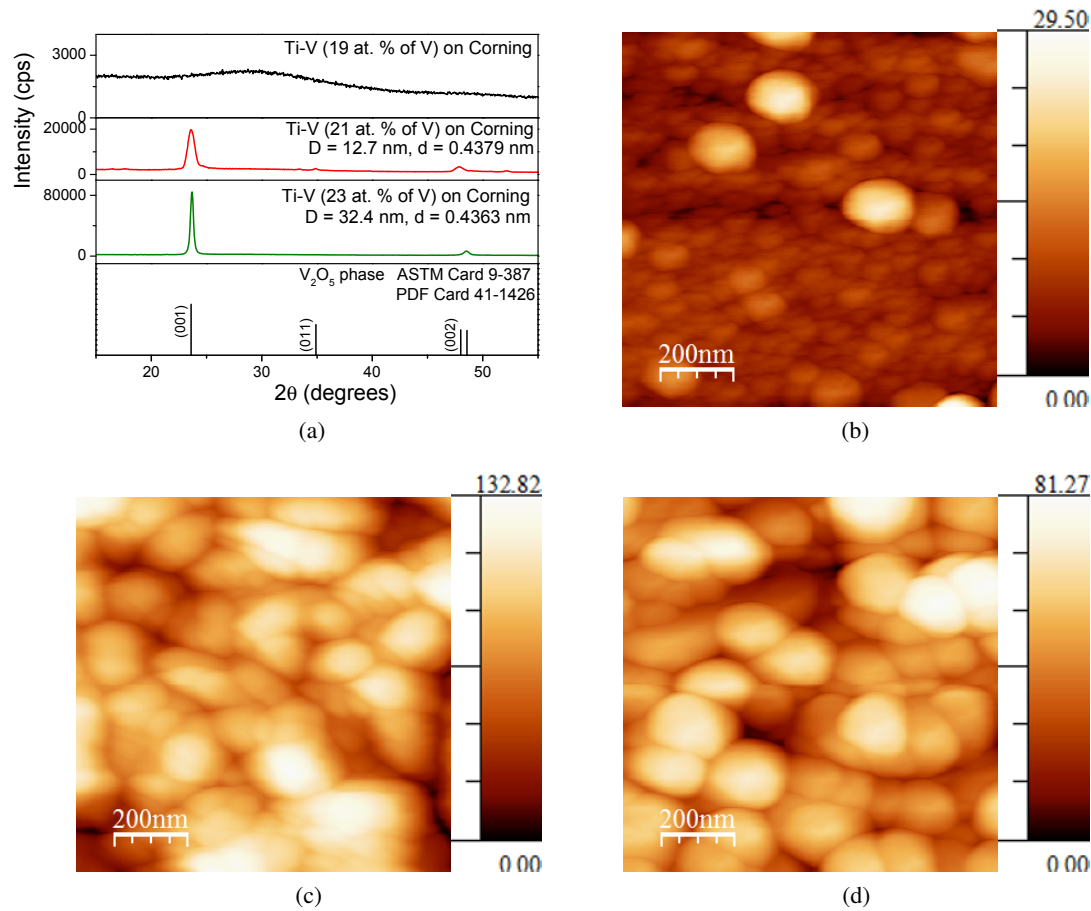
Fig. 1. Results of XRD measurements of Ti–V oxides according to the standard pattern for V_2O_5 phase (a) and AFM images of Ti–V oxides with vanadium addition of 19 at. % (b), 21 at. % (c), 23 at. % (d).
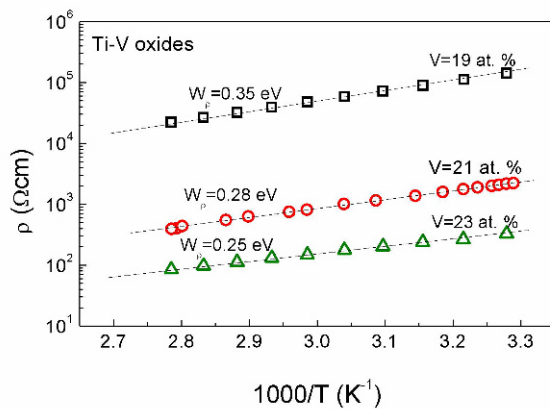

Fig. 2. Results of d.c. resistivity vs. temperature dependence of measured Ti-V oxide thin films.

spectra, dispersion characteristics of refractive index vs. wavelength have been calculated (Fig. 4d).

The highest value of refractive index (n = 2.56 at 550 nm) was obtained for Ti–V oxides with 23 at. % of vanadium. Values of thickness calculated for the thin films varied between samples with different amounts of vanadium. The thinnest layer (ca. 334 nm) was obtained for vanadium amount of 19 at. %, while Ti–V oxides with 21 and 23 at. % of vanadium were ca. 415 and 470 nm thick, respectively.

Hardness of nanocrystalline Ti–V oxide thin films with different amounts of V was measured using a force of 2 mN, which was equivalent to the physical thickness of examined films. Based on recorded data, hardness (H) and reduced elastic modulus (E_r) were estimated. In Fig. 5, the images of Ti–V oxide thin films surfaces after the hardness measurements have been presented. The shape of
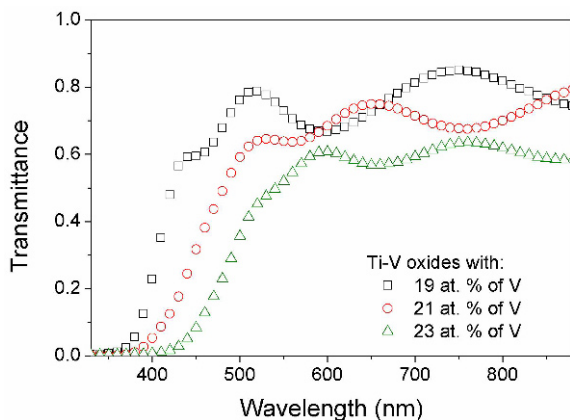
Fig. 3. Transmittance spectra of Ti–V oxide thin films with vanadium addition of 19, 21 and 23 at. %

the indents made in thin oxide films is also shown. Two-dimensional profiles of the contact depth have been presented in Fig. 6.

It seems that the structure and amount of vanadium influence the hardness of Ti–V oxides. The Ti–V oxide thin films doped with addition of 19 at. % of V had the highest hardness of 6.3 GPa, while incorporation of larger amount of V decreased it. The lowest hardness of 5.4 GPa was obtained for Ti–V oxide thin films with 21 at. % of V. According to XRD results, Ti–V oxide thin films with 19 at. % of V were amorphous, while V_2O_5 phase was observed in case of thin films containing 21 and 23 at. % of V. In comparison to hardness results, it seems that V_2O_5 phase decreases the hardness value in comparison to amorphous thin films. The hardness of amorphous thin films is ca. 25 % higher than that for standard soda-lime glass [26, 27]. In case of thin films with V_2O_5 phase, hardness is comparable.

The highest contact depth (Fig. 6) has been observed in case of Ti–V oxide thin films with 21 at. % of vanadium, while the lowest was obtained for Ti–V oxide with 19 at. % of V. The increase in contact depth indicates the decrease in hardness of the thin oxide films if the load applied to the nanoindenter tip during the measurement is the same. Additionally, the results of investigation with the nanoindenter have revealed that there is only a slight change in the value of reduced elastic modulus in case of Ti–V oxide thin films. For

thin films with 19 at. % of vanadium the results are very beneficial since the hardness has increased in comparison to other samples, but the reduced elastic modulus remained at similar level. The results of hardness and reduced elastic modulus of Ti–V oxide thin films have been presented in Fig. 7 and collected in Table 1. The presented results were averaged from 10 tests for each sample.

Table 1. Results of hardness and reduced elastic modulus measurements of Ti–V oxide thin films.

Ti-V oxides (at. % of V)	Hardness H (GPa)	Reduced elastic modulus E_r (GPa)
19	6.3	75.0
21	5.4	77.9
23	5.6	74.4

In Fig. 8, results of contact angle investigation carried out with water, ethylene glycol and ethanol for Ti–V oxide thin films with different amount of V have been presented. The highest contact angle was obtained for Ti–V oxide doped with 19 at. % of vanadium. With increased amount of V to 21 and 23 at. % the contact angle has decreased. There was no meaningful difference between water contact angle for Ti–V oxides with 21 and 23 at. % of V. Ethanol contact angle decreased with the increase of vanadium addition. The contact angle values were also dependent on surface energy of the applied liquids. The highest contact angle values were recorded for water, which is a polar liquid with much higher surface energy than ethylene glycol or ethanol. The lowest values of contact angle were obtained for ethanol, which simultaneously has the lowest surface tension. What is worth to emphasize, Ti–V oxide thin film with addition of 19 at. % of vanadium is the only film which is hydrophobic with the water contact angle of approximately 93.9 degrees. Thin films doped with 21 and 23 at. % of V are hydrophilic and the water contact angle is much lower than 90 degrees.

In Fig. 9, Zisman plot and critical surface tensions of Ti–V oxide thin films have been presented. The values of critical surface tension have been calculated using Zisman approach [28]. The results of
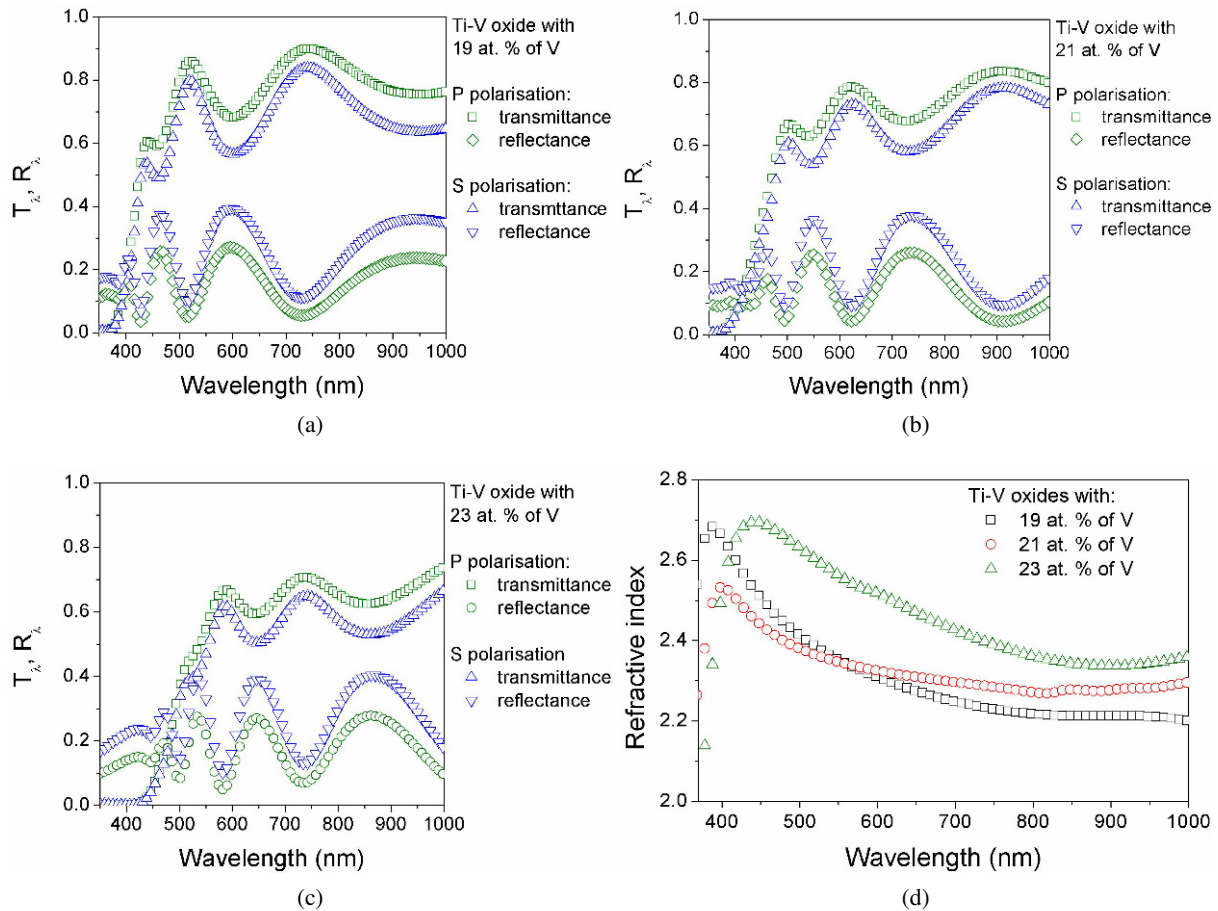
Fig. 4. Transmittance and reflectance spectra of as deposited nanocrystalline Ti–V oxides thin films with addition of 19 at. % (a), 21 at. % (b), 23 at. % (c) of V and refractive index characteristics of Ti–V oxides.

calculations have shown, that in case of thin films with 19 and 21 at. % of V, critical surface tension is equal. Increasing V amount to 23 at. % results in two-times increase in critical surface tension. Images of droplets of different liquids on the samples surfaces and results of measurements of contact angle and critical surface tension of Ti–V oxide thin films are shown in Table 2.

The influence of the amount of V on surface free energy of Ti–V oxide thin films was determined using geometric and harmonic mean approaches. In geometric mean approach (Fig. 10a), the values have been estimated according to Fowkes approach [29], using Owens and Wendt equations. In harmonic mean approach, the values of surface free energy have been estimated using Wu equations (Fig. 10b).

Surface free energy is more than two-times lower in case of Ti–V oxide thin film with 19 at. % in comparison to that with 21 and 23 at. % of V, which indicates that its surface is much less wettable. The surface free energy for Ti–V oxide thin film (19 at. % of V) calculated by geometric and harmonic approach is equal to 18.7 and 22.5 mN/m, respectively. In geometric approach the dispersive part is the main component of total surface free energy, while in harmonic approach the dispersive and polar components are equal.

In case of Ti–V oxide thin films (21 and 23 at. %), the surface free energies were almost the same and equal to approximately 47 mN/m. In both cases, total values of surface free energies were mainly dependent on dispersive component. Contribution of polar component was below 25 %
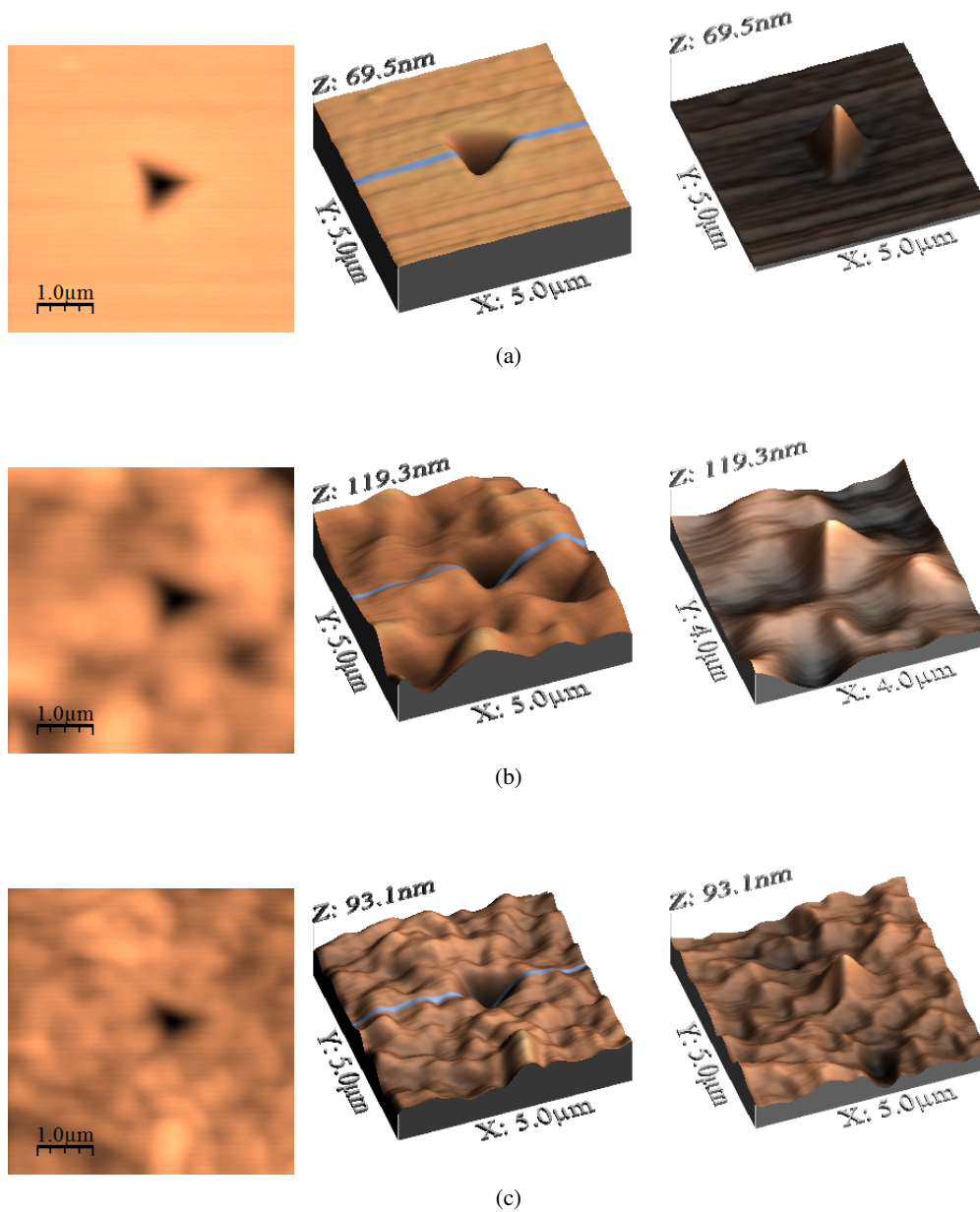
Fig. 5. Images of indents and shapes of the indents made during nanoindentation of Ti–V oxide thin films doped with 19 at. % of V (a), 21 at. % of V (b) and 23 at. % of V (c).

of total value. The results show that the increase of vanadium amount results in an increase in the total value of surface free energy.

4. Discussion

It seems that there is a correlation between the properties of prepared thin films and the amount of V addition. Dependence of average transmission and resistivity on the amount of vanadium addition in Ti–V oxide thin films has been presented in Fig. 11. With the increase of vanadium there is a simultaneous decrease of transmission and resistivity. The change in incorporated vanadium from 19 to 21 at. % causes a little change of the average transmission from ca. 75 % to 70 %, however,

Table 2. Results of contact angle and critical surface tension investigations of Ti–V oxide thin films.

at. % of V in thin films	Contact angle θ (degrees)			Critical surface tension (mN/m)
	water	ethylene glycol	ethanol	
19	93.9 ±2.8	77.9 ±3.5	33.9 ±6.4	10.2
21	55.8 ±1.4	45.8 ±5.1	22.1 ±2.9	10.2
23	55.0 ±3.6	41.7 ±2.8	9.6 ±1.9	19.5

Fig. 6. Contact depth two-dimensional profiles of Ti–V oxide thin films doped with 19 at. %, 21 at. % and 23 at. % of V.

the change of resistivity is more meaningful and is equal to $1.4 \cdot 10^5$ and $2.1 \cdot 10^3$ Ωcm, respectively. Further increase of vanadium amount from 21 to 23 at. % causes a significant decrease of average transmission down to 60 %, while the resistivity decreases only to $3.3 \cdot 10^2$ Ωcm. It can be assumed, that incorporation of larger amount of vanadium would greatly deteriorate the average transmission and hardly decrease the resistivity of the thin films.

Hardness and reduced elastic modulus are dependent on the structure and amount of vanadium in Ti–V oxide thin films. Ti–V oxide with addition of 19 at. % of V is amorphous and exhibits the highest hardness, of about 6.3 GPa, for all measured samples. Thin films with addition of 21 and 23 at. % of vanadium have nanocrystalline V_2O_5 structure with crystallites sizes of 12.7 and 32.4 nm, respectively and exhibit much lower hardness (of ca. 20 %) in comparison to Ti–V oxide with amorphous phase. However, the reduced elastic modulus remains at the similar level of ca. 75 GPa for all measured thin films. Higher hardness and similar reduced elastic modulus of Ti–V oxide with 19 at. % of V makes this thin film interesting from the application point of view as for example the coatings for organic materials. Comparison of the structure, amount of vanadium addition, hardness and reduced elastic modulus has been shown in Fig. 12.

(a)

(b)

Fig. 7. Influence of vanadium amount on hardness (a) and reduced elastic modulus (b) of Ti–V oxide thin films.
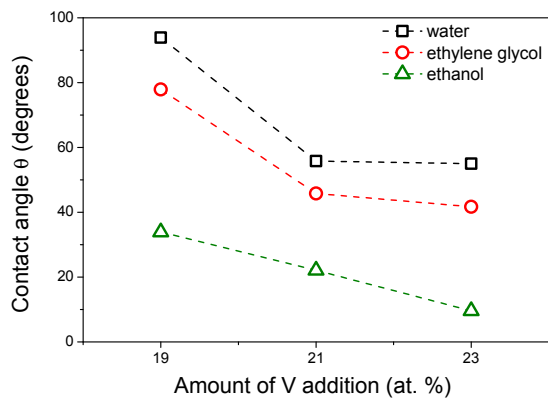

Fig. 8. Contact angle values of Ti–V oxide thin films with different amounts of V measured for water, ethylene glycol and ethanol.
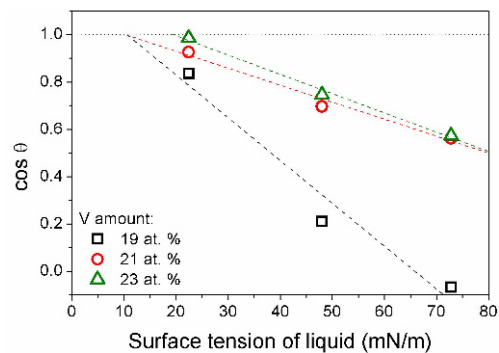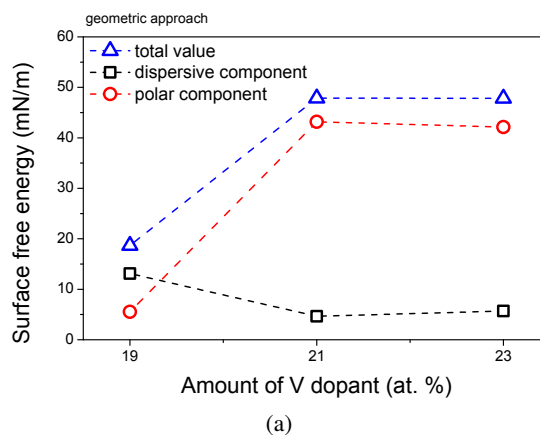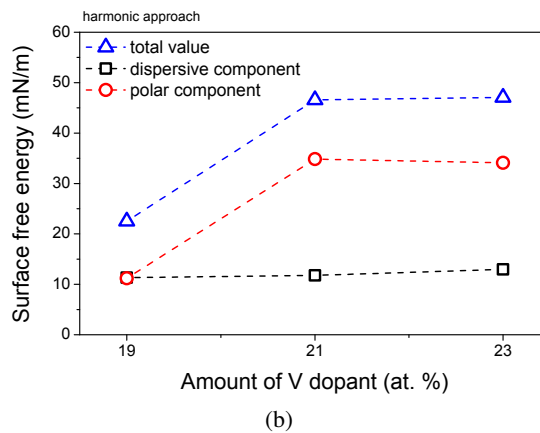

Fig. 9. Zisman plot of critical surface tension of Ti–V oxide thin films with different amounts of V addition.

(a)

(b)

Fig. 10. Results of surface free energy investigation of Ti–V oxide thin films estimated according to Fowkes approach using Owens and Wendt equations (geometric mean approach) (a) and Wu equations (harmonic mean approach) (b).
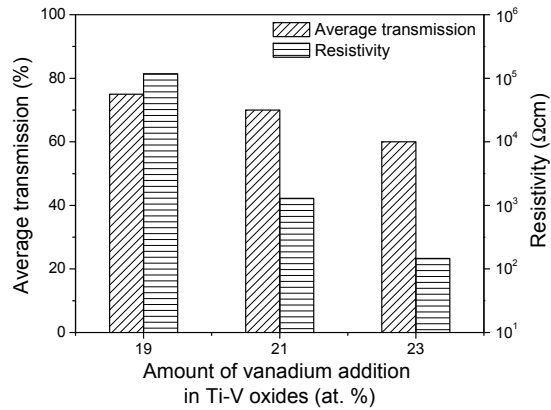
Fig. 11. Comparison of average transmission and resistivity results for Ti–V thin oxide films in terms of amount of vanadium addition.
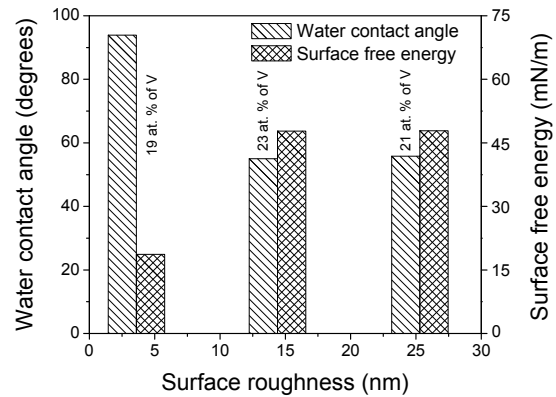

Fig. 12. Comparison of hardness and reduced elastic modulus results for Ti–V thin oxide films in view of their structure phase.

Fig. 13. Comparison of water contact angle and surface free energy results for Ti–V thin oxide films in terms of their surface roughness.

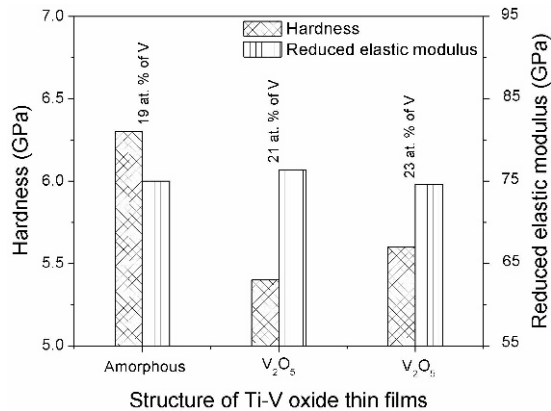Wettability of the thin films strongly depends on their surface properties e.g. roughness. In case of amorphous phase determined for Ti–V oxides with 19 at. % of vanadium, the lowest value of surface roughness of ca. 3.6 nm has been determined. Simultaneously, the highest water contact angle (93.9º) and the lowest surface free energy (ca. 20 mN/m) have been observed, what can be related to the very smooth surface. Moreover, in case of V_2O_5 phase, which occurred in thin films with 21 and 23 at. % of vanadium, the surface roughness increased meaningfully to 25.3 and 14.4 nm, respectively. Water contact angles of these thin films (ca. 55º) were much lower and the surface free energies (ca. 47 mN/m) were much higher

in comparison to Ti–V oxide with 19 at. % of V, which also can be related to rougher surface. In Fig. 13, a comparison of surface roughness and wettability of investigated thin films has been presented.

5.   Conclusions

The Ti–V oxide thin films containing 19, 21 and 23 at. % of vanadium were prepared using high energy reactive magnetron sputtering process. XRD results showed that Ti–V oxides with 19 at. % addition of vanadium were amorphous, while an increase in vanadium content up to 21 and 23 at. % resulted in formation of V_2O_5 phase with crystallites sizes of 12.7 and 32.4 nm, respectively. AFM investigations also showed that incorporation of 19 at. % of vanadium resulted in the smallest average grain size and surface roughness among the prepared samples, which seems to confirm XRD results.

The prepared samples exhibit high transmission of ca. 75, 70 and 60 % in the visible light range for Ti–V oxides with 19, 21 and 23 at. % of V. With the increase of vanadium addition, the red shift of the cutoff wavelength has occurred. The resistivity of the samples is in the range of $3.3 \cdot 10^2 - 1.4 \cdot 10^5$ and it decreases with the increase of vanadium addition. The prepared Ti–V oxide thin films belong to the special group of transparent oxide semiconductors due to high transmission and proper resistivity val-

ues. As it can be seen, the highest transmission as well as the highest resistivity was determined for Ti–V with 19 at. % of vanadium addition. In contrary, the lowest transmission and the lowest resistivity was obtained in case of Ti–V oxide with the largest addition of vanadium.

Hardness of Ti–V oxides was determined with the aid of nanoindentation technique. The highest hardness of 6.3 GPa was determined in case of Ti–V oxide thin films with 19 at. % addition of vanadium and it was about 25 % higher than the corresponding value for common soda lime glass. In case of the samples with 21 and 23 at. % of vanadium, hardness remained at the similar level of 5.4 – 5.6 GPa. The reduced elastic modulus of investigated thin films was similar for all the samples and was in the range of 74.4 – 77.9 GPa.

Wettability of thin films showed hydrophobic behavior of Ti–V oxide with vanadium addition of 19 at. %, while hydrophilic behavior was observed in case of thin films with vanadium addition of 21 and 23 at. %. The contact angle for water was 93.9, 55.8 and 55.0º for Ti–V oxides with vanadium addition of 19, 21 and 23 at. %, respectively. Ti–V oxide thin film with 19 at. % of vanadium addition had the lowest surface free energy, while for oxides with 21 and 23 at. % of vanadium, the surface free energy was more than two times higher. It indicated, that the surface of Ti–V oxide with 19 at. % of V was much less wettable.

Ti–V oxide thin film with 19 at. % of V could find application as a protective, hydrophobic and transparent p-type semiconductor whereas the thin films with 21 and 23 at. % of vanadium could be applied as transparent n-type semiconductors. In the future, simultaneous use of these thin films with different types of electrical conduction could find application in transparent electronic devices, such as e.g. diodes.

Acknowledgements

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