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STRUCTURAL AND OPTICAL PROPERTIES OF VO_x THIN FILMS

WŁASNOŚCI STRUKTURALNE I OPTYCZNE CIENKICH WARSTW VO_x

VO_x thin films were deposited on Corning glass, fused silica and Ti foils by means of rf reactive sputtering from a metallic vanadium target. Argon-oxygen gas mixtures of different compositions controlled by the flow rates were used for sputtering. Influence of the oxygen partial pressure in the sputtering chamber on the structural and optical properties of thin films has been investigated.

Structural properties of as-sputtered thin films were studied by X-ray diffraction at glancing incidence, GIXD. Optical transmittance and reflectance spectra were recordedwith a Lambda 19 Perkin-Elmer double spectrophotometer. Thickness of the films was determined from the profilometry. It has been confirmed by XRD that the deposited films are composed mainly of V_2O_5 phase. The estimated optical band gap of 2.5 eV corresponds to V_2O_5.

Keywords: VO_x thin films, reactive sputtering, microstructure, optical properties, energy band gap

Cienkie warstwy VO_x były nanoszone na szkło Corning metodą rozpylania magnetronowego rf. Jako katody użyto metalicznego wanadu. Były one nanoszone w komorze wypełnionej mieszaniną argonu i tlenu w różnych proporcjach przy ustalonych przepływach. Zbadano wpływ ciśnienia parcjalnego tlenu w komorze na własności strukturalne i optyczne otrzymanych warstw.

Własności strukturalne cienkich warstw zostały określone metodą rozpraszania promieniowania rentgenowskiego padającego pod małymi kątami (GIXD). Widma optyczne transmitancji i odbicia zostały wykonane przy użyciu spektrometru Lambda 19 Perkin-Elmer. Grubość badanych warstw zmierzono za pomocą profilometru.

Pomiary XRD potwierdziły, że otrzymane warstwy składają się głównie z fazy V_2O_5. Wyznaczona optycznie przerwa energetyczna wynosząca 2.5 eV odpowiada przerwie energetycznej V_2O_5.

1. Introduction

Vanadium has various valence states and exists in a number of oxide forms of vanadium oxide. There are at least 15 different vanadium oxides reported till now, such as VO, V_2O_3, VO_2, V_2O_5, V_6O_{13} and so on. Vanadium oxide thin films have been widely studied for optical, electrical, electrochemical, thermo-chromic and thermal switching materials [1-11]. The interest in these materials has increased in the last few years due to their potential scientific and technological applications, for example as a catalyst [12], a window for solar cells [13], electrochromic devices [14], electronic information displays [15] and color memory devices [16, 17].

The structural changes of vanadium thin films are of vital importance for their practical applications. The aim of this paper was determine the structural and optical properties of vanadium oxide thin films deposited by rf reactive sputtering. The influence of gas atmosphere during deposition on the microscopic structure, morphology and the band gap of the films has been studied.

Numerous techniques have been used for preparing vanadium oxide thin films such as:

- sol-gel [18],
- electrochemical [19],
- vacuum deposition techniques including plasma-enhanced chemical vapour deposition (PECVD) [20],
- pulsed laser deposition [21],
- thermal evaporation technique [22],
- atomic layer deposition [23],
- reactive magnetron sputtering [24-26],
- rf sputtering deposition [27-30].

From thin film deposition methods listed above, the reactive process, i.e. the sputtering rf the metallic target under oxidizing controlled atmosphere permits greater control over deposition parameters and provides an important fabrication approach for optimization. Moreover, reactive sputtering provides thin films that are dense and uniform in thickness and which is very important, in case of VO_x, is available to control the film stoichiometry, x.

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2. Experimentaldetails

2.1. Thin film deposition

Vanadium oxide thin films have been deposited by rf reactive sputtering from metallic V target in Ar+O_2 flow controlled gas atmosphere. Corning glass and fused silica served as substrates. Deposition process was carried out under predefined conditions of the total gas pressure, varied oxygen (within range: 0.3-2.1 sccm) and constant argon (6.7 sccm) flows rates, constant input power (280-290 W) and voltage (1150V) as well as the controlled substrate temperature (560 K). Prior to the sample deposition, the target pre-sputtering in Ar + O_2 atmosphere was performed in order to stabilize the sputtering conditions (voltage, pressure, gas composition) and to equilibrate the oxidized target surface. Deposition conditions of the thin films are collected in Table 1.

TABLE 1
Comparative data of thin films: deposition conditions, thickness, bandgap

	VOx1	VOx2	VOx3
flow(Ar) during deposition	6.7	6.7	6.3
flow(O_2) during deposition	2.1	0.7	0.3
input power [W]	290	280	290
rf voltage (U_{rf}) during deposition [V]	1150	1150	1150
Ar+O_2 pressure [mbar]	$4.7 \cdot 10^{-2}$	$4.3 \cdot 10^{-2}$	$4.1 \cdot 10^{-2}$
time of deposition [min]	240	240	240
film thickness [nm]	431±28	421±43	420±49
band gap [eV] from optical transitions m = 2	2.21±0.05	2.47±0.05	2.42±0.05

2.2. XRD analysis

The crystallographic studies were carried out by means of X-ray diffraction at grazing incidence (GID) with X'Pert Philips diffractometer within the range of diffraction angles 2θ from 20 deg to 80 deg with the CuK_α filtered radiation.

2.3. SEM and EDS

The images of microstructure of the films were studied using the scanning electron spectroscopy (SEM) technique (Nova 200 NANOsem, Fei Company). An energy dispersive X-ray spectrometer (Oxford Instruments) coupled with scanning electron microscope was used to determine the chemical composition of the samples. The analysis was focused on vanadium distribution.

2.4. Optical spectroscopy

Optical transmittance and reflectance spectra over a wide wavelength range from 180to3200nm were measured with Lambda 19 Perkin-Elmer double beam spectrophotometer equipped with a 150 mm integrating sphere. The band gap energy E_g of a semiconductor can be evaluated from the experimentally measured transmittance T and reflectance R within the range of the fundamental absorption.

2.5. Thin film thickness

The thickness of the films was measured using Bruker's DektakXT^{TM}Stylus Profiler.

3. Results and discussion

Majority of films prepared by the reactive sputtering show only weak crystallization. Special care has to be taken to improve the crystallization conditions. Therefore, only GID patterns have been presented and discussed in this paper **Fig. 1** demonstrates X-ray diffraction patterns of as sputtered VO_xthin films. The experimental data were interpreted using XRD patterns distributed by the International Centre for Diffraction DATA –ICDD. As can be seen VOx3 film is weakly crystallized. From the other hand, films VOx1and VOx2 are much better crystallized. X-ray phase analysis confirmed that all peaks correspond to the V_2O_5 orthorhombiccompound.

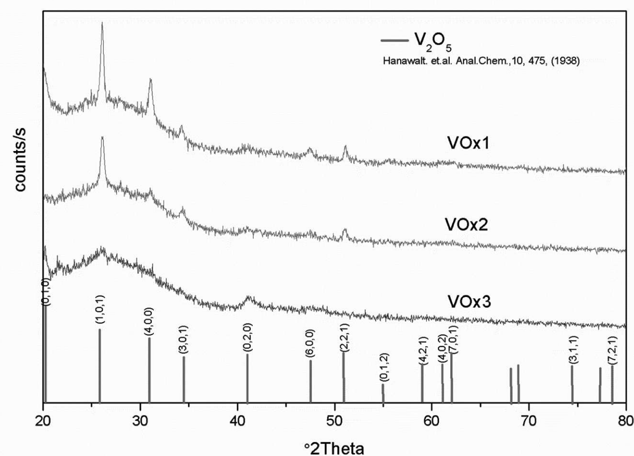

Fig. 1. XRD patterns of the as-sputtered thin films

Typical SEM micrographs of the films are illustrated in **Figs. 2-4a-d.**The obtained results show that morphology of the films differ substantially. VOx1films are composed fromelongated ribbons of 800 nm lengths and 200 nm width. Films VOx2 exhibit shorter sizes of the ribbons 200-350×60 nm. The flower-like morphology of the diameter ca. 250 nm show films VOx3. Presented in Figs. 2-4 e, EDS chemical analysis apart of the corning support elements, only V and O can be detected as a elements coming of the film. According to the EDS (Figures 2-4 e) detailed analysis taken at different places on film surface, the distribution of V and O both elements is homogenous.

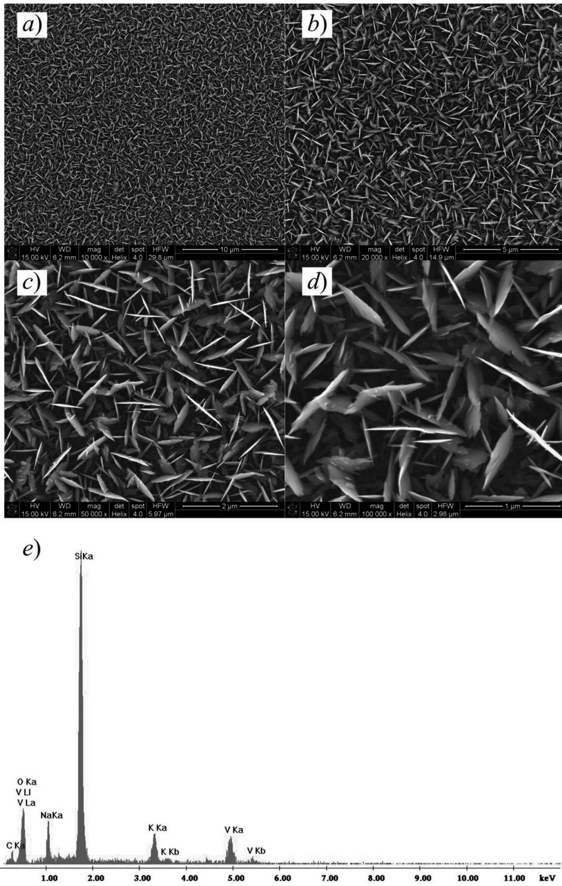

Fig. 2. a-d: Typical SEM images of the as-sputtered thin films; e: EDS spectrum for VOx1 sample

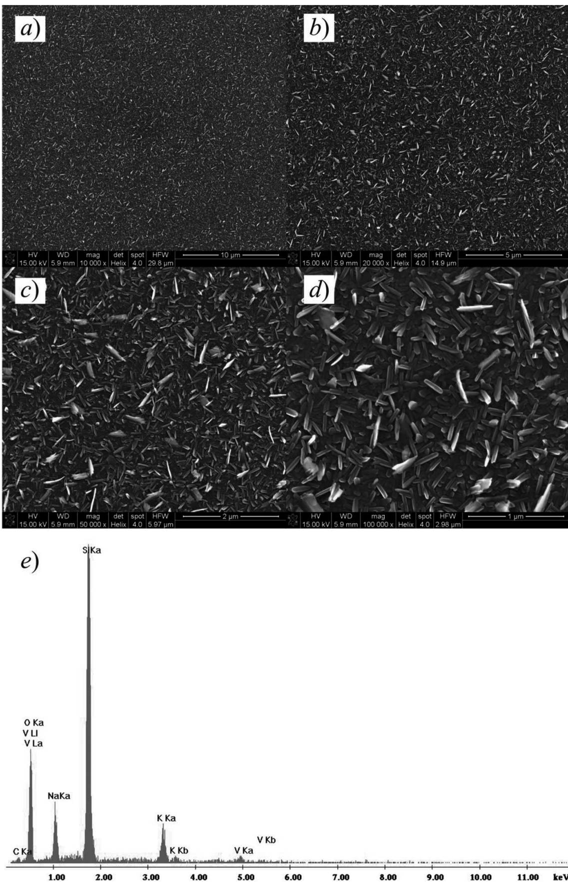

Fig. 3. a-d: Typical SEM images of the as-sputtered thin films; e: EDS spectrum for VOx2 sample

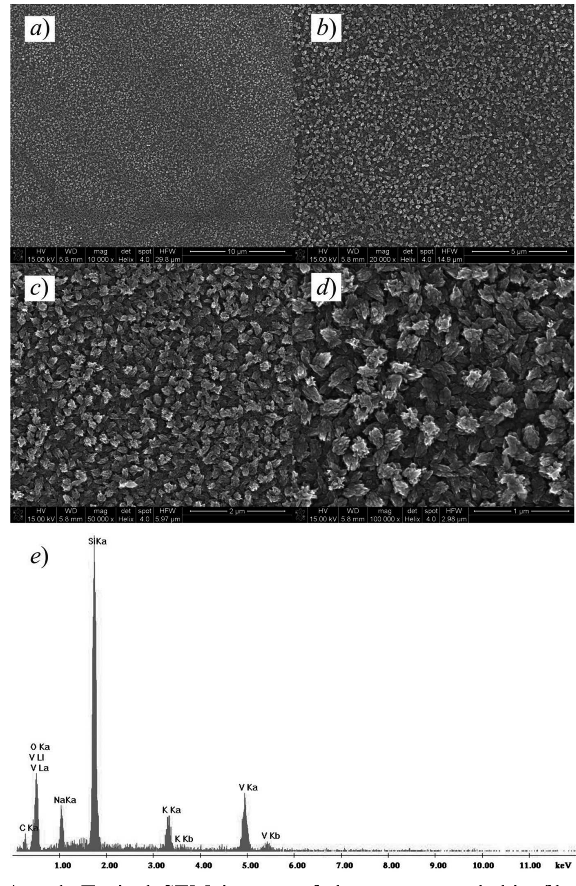

Fig. 4. a-d: Typical SEM images of the as-sputtered thin films; e: EDS spectrum for VOx3 sample

The average mean crystallite size of the materials was calculated from Scherrer's equation [31]

$$\lambda\beta\theta \mathrm{d}_{\mathrm{XRD}}=\frac{\mathrm{K}}{\cos} \qquad (1)$$

Where, d_{XRD} is the crystallite size, λ – is the wavelength of the X-ray radiation (CuK_{α} = 0.1540598 nm), K is constant equal to 0.89 and β is the line broadening at the half-maximum intensity aftersubtraction of equipment broadening. The average crystallite size was: 53 and 52 nm for VOx1 and VOx2, respectively. The obtained d_{XRD} arein relatively good agreement with SEM measurements.

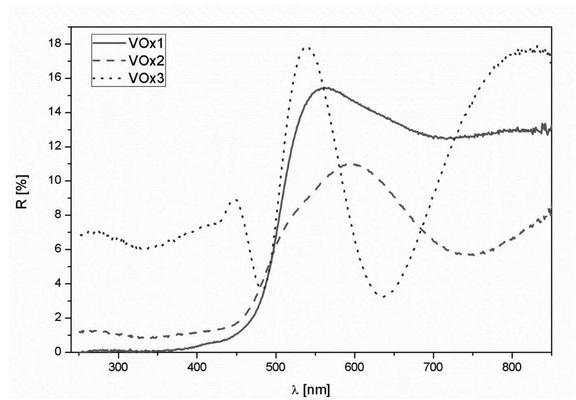

Fig. 5. Reflectance spectra for VOx1, VOx2, VOx3 thin films

Fig. 5 demonstrates reflectance spectra of studied films. The spectra ofVOx1 and VOx2 show similar character. Wide

maximum and minimum is observed at λ range of 550-600 nm and ca 750 nm, respectively. The spectrum of VOx3 is much complex. The optical refractive index, n, has been determined from the experimental data presented in Fig. 5. Assuming that the excitation coefficient is negligible [32] we have:

$$R = \frac{(n-1)^2}{(n+1)^2} \quad (2)$$

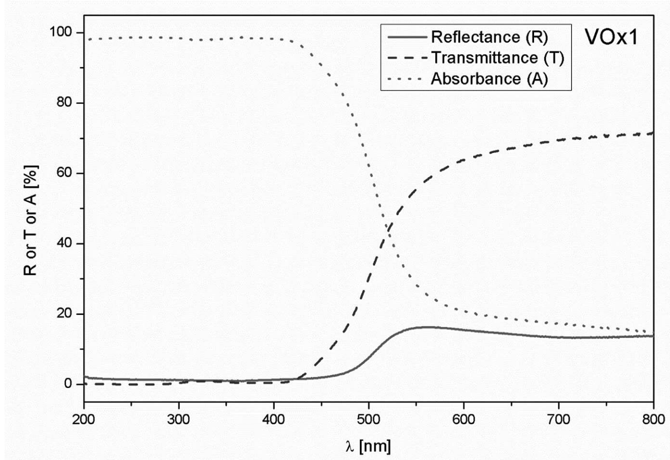

Fig. 6. Reflectivity index as a function wave length for VOx1, VOx2, VOx3 and Maki et al. [34] results for V_2O_5 thin film prepared by reactive magnetron sputtering

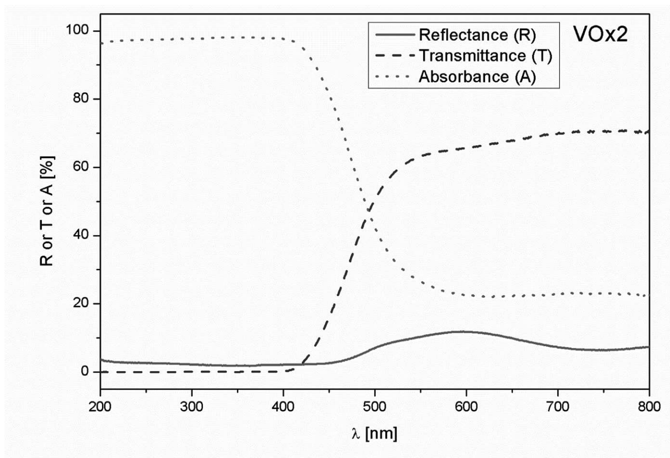

Fig. 7. Reflectance (R), transmittance (T) and absorbance (A) spectrafor VOx1 film

Figs. 6-8 demonstrate reflectance (R), transmittance (T) and absorbance (A) spectra of VOx1, VOx2 and VOx3, respectively. Again, both samples VOx1, VOx2 show similar dependencies. Absorption coefficient α is expressed by:

$$\alpha = \frac{1}{d}\ln\left(\frac{(1-R)^2}{T}\right), \quad (3)$$

whered is film thickness. **Fig. 9** show dependence of α on photon energy hν for VOx1 sample.

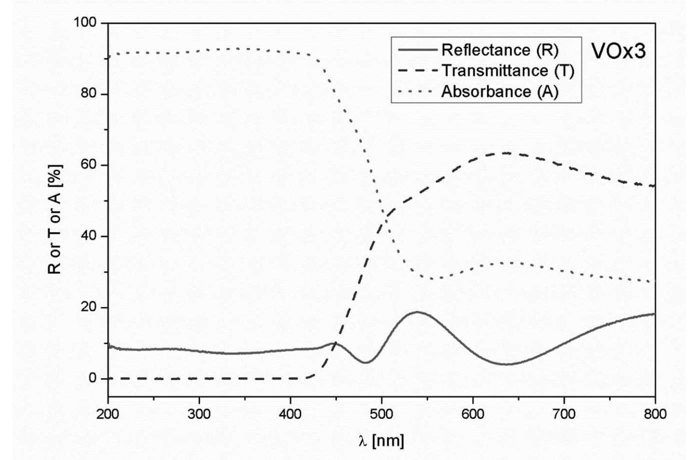

Fig. 8. Reflectance (R), transmittance (T) and absorbance (A)spectra forVOx2 film

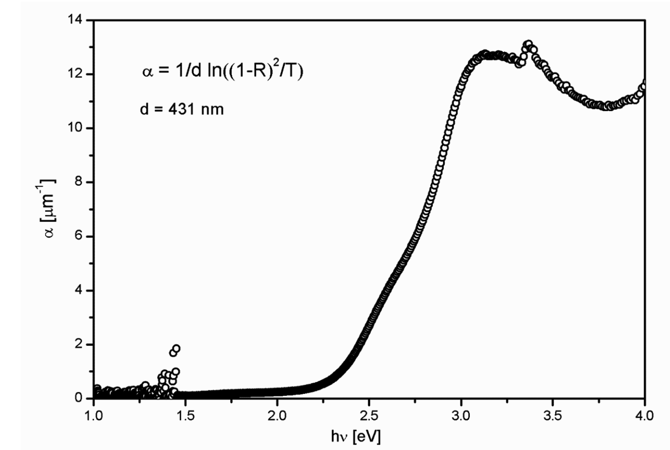

Fig. 9. Reflectance (R), transmittance (T) and absorbance (A) spectra forVOx3 film

The value of E_g can be found from the plot of $(\alpha h\nu)^{1/m}$ as a function of the photon energy hν; α is the absorption coefficient:

$$\alpha h\nu = a(h\nu - E_g)^m_, \quad (4)$$

where a is a constant. The power coefficient m takes a value of 1/2, 3/2, 2 or 3 depending on the type of transition: direct allowed, direct forbidden, indirect allowed or indirect forbidden, respectively.

Equation 3 as well as 4 are only valid over the high absorption region, where, in the case of thin films, transmittance and reflectance spectra do not show any interference effects. The band gap E_g is determined by extrapolating the linear part of the fit $(\alpha h\nu)^{1/m}$ versus hν. In case of the amorphous non-metallic materials Eq 4 gives the best fit with m=2.

The examples of this methodfor m=1/2 and m=2are shown in **Figure 10**. Determined band gap values are collected in Table 1. The presented results E_g are close to that reported by Maki et al [34]: 2.25 eV, determined to V_2O_5 thin film, deposited by magnetron sputtering and then annealed at 500°C in oxygen atmosphere. They are also close to the results reported by Li-Jang Meng et al. [25] obtained for V_2O_5 thin film deposited by magnetron sputtering: 2.16-2.59 eV (substrate temperature: 400°C and room temperature, respectively).

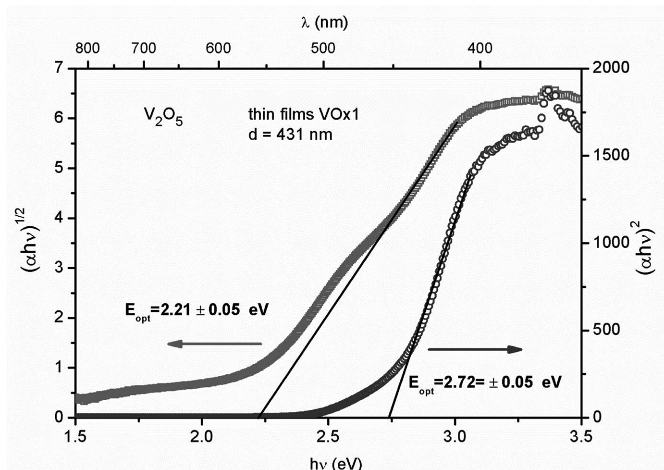

Fig. 10. Absorption coefficient α versus (hν) for thin filmVOx1

4. Conclusions

In this paper the main structural and optical characteristics of vanadium oxide thin films were studied. Films were deposited by means rf reactive sputtering. The effect of oxygen concentration during deposition on structural and optical properties has been observed. At higher oxygen concentration the as-sputtered films are well crystalized. According to XRD analysis they crystalize as V_2O_5 orthorhombic phase. Determined refractive index varies values 1.6-2.3 within 500-800 nm of wavelength. The optical bandgapassumes value 2.21-2.47 eV.

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REFERENCES

[1] E.E. Chain, Appl. Optics **30**, 2782-2787 (1991).
[2] R.T. RejendraKumar, B. Karunagaran, D. Mangalaraj, S.K. Narayandass, P. Manoravi, M. Joseph, V. Gopal, Sensors and Actuators A **107**, 62-67 (2003).
[3] P. Liu, S-H Lee et al., Solid State Ionics **165**, 223-228 (2003).
[4] X. Chen, Q. Lv, X. Yi, Optik **123**, 1187-1189 (2012).
[5] A. Löfberg, T. Giornelli, S. Paul, E. Bordes-Richard, Applied catalysis A: General **391**, 43-51 (2011).
[6] S.P. Price, X. Tong et al., Surface Science **605**, 972-976 (2011).
[7] S. Liu, J. Wu et al., Journal of Molecular Catalysis A: Chemical **332**, 84-92 (2010).
[8] R. Mitdank, D. Habel et al., Nuclear Instruments and Methods in Physics Research B **269**, 345-352 (2011).
[9] M.Y. Song, S. Chin et al., Ceramics International **38**, 2613-2618 (2012).
[10] S. Zhuikov, W. Wlodarski, Y. Li, Sensors and Actuators B **77**, 484-490 (2001).
[11] A. Cabota, J. Arbiola, A. Corneta, J.R. Morantea, F. Cheng, M. Liu, Thin Solid Films **436**, 64-69 (2003).
[12] C.O. Park, S.A. Akbar, J. Hwang, Mater. Chem. Phys.**75**, 55-60 (2002).
[13] B.W. Licznerski, K. Nitsch, H. Teterycz, T. Sobanski, K. Wisniewski, Sensors and Actuators B **103**, 69-75 (2004).
[14] C.O. Park, S.A. Akbar, J. Hwang, Mater. Chem. Phys.**75**, 55-60 (2002).
[15] M. Radecka, M. Rekas. K. Zakrzewska, Trends in Inorganic Chemistry **9**, 81-126 (2006).
[16] G. Zhao, H. Kozuka, H. Lin, T. Yoko, Thin Solid Films **339**, 123-128 (1999).
[17] R.K. Karn, M. Misra, O.N. Srivastava, Int. J. Hydrogen Energy **25**, 407-413 (2000).
[18] J. Livage, D. Ganguli, Solar Energy Materials and Solar Cells **68**, 365-381 (2001).
[19] P. Liu, S-H Lee et al., Solid State Ionics **165**, 223-228 (2003).
[20] J.G. Zhang, P. Liu, J.A. Turner, C.E. Tracy, D.K. Benson, J. Electrochem. Soc. **145**, 1889-1892 (1998).
[21] Y.L. Wang, X.K. Chen et al., Surface & Coatings Technology **201**, 5344-5347 (2007).
[22] X. Wu, F. Lai, L. Lin, Y. Li, L. Lin, Y. Qu, Z. Huang, Applied Surface Science **255**, 2840-2844 (2008).
[23] P. Dagur, A.U. Mane, S.A. Shivashankar, Journal of Crystal Growth **275**, e1223-e1228 (2005).
[24] Y. Wang, M.C. Li, L.C. Zhao, Surface & Coatings Technology **201**, 6772-6776 (2007).
[25] L-J. Meng, R.A. Silva et al., Thin Solid Films **515**, 195-200 (2006).
[26] V. Melnik, I. Khatsevych, V. Kladko, A. Kuchuk, V. Nikirin, B. Romanyuk, MaterialsLetters**68**, 215-217 (2012).
[27] S.P. Lim, J.D. Long et al., Journal of Physics D: Applied Physics **40**, 1085-1090 (2007).
[28] A. Gies, B. Pecquenard, A. Benayad, H. Martinez, D. Gonbeau, H. Fuess, A. Lavasseur, SolidStateIonics **176**, 1627-1634 (2005).
[29] J. Liu, X. Wang, Q. Peng, Y. Li, Sensors and Actuators B **115**, 481 (2006).
[30] K. Schneider, J. Drogowska, A.G. Balogh, Z. Tarnawski, N.-T.H. Kim-Ngan, K. Zakrzewska, VO_x thin films deposition by reactive rf sputtering, Reactivity of Solids, K. Przybylski, Ed, Polish Ceramic Society, Krakow 2013. P. 305-314.
[31] H. Ogawa, A. Abe, M. Nishikawa, S. Hayakawa, J. Electrochem. Soc. **128**, 685-689 (1981).
[32] G. Shankar, P.S. Joseph, M. Yosuva Suvakin, A. Sebastiyan, Physica B **405**, 4231 (2010).
[33] K. Maki, T. Fukuda, H. Momose, T. Nakano, S. Baba, J. Fac. Sci. Tech., SeikeiUniv. **49**, 41-44 (2012).

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