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Technology and application of transition metal oxide of W-V-O as functional layers and NiO thin films as counter electrode material in electrochromic "Smart Windows"

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Abstract

The present study is related to preparation and investigation of mixed W-V-O films, deposited on conductive glass substrates by atmospheric pressure chemical vapor deposition. The presence of lower-temperature precursor $V(CO)_6$ lead to faster growing of the mixed oxide film. The results show two times higher growth-rate compared to single oxide of WO_3. The color efficiency calculated is 20 cm^2/C, optical modulation 65.2%. Vibrational spectra studied by Raman and FTIR spectroscopy show Raman peaks and absorption bands revealing monoclinic WO_3 and orthorhombic V_2O_5 phases, separately existing in the mixed oxide film structure. The surface morphology is observed by AFM. Films transmittance and reflectance characterization are performed. For the counter electrode in the EC, NiO films are deposited electrochemically. The UV-VIS-NIR optical measurements performed in the spectral range of 300 - 1000 nm show that films possess transmittance in the range of 70% - 85%. This high transmittance of the counter electrode film would contribute to the needed high initial optical transmittance of the "smart window".

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1. Introduction

An electrochromic (EC) device is an optical system consisting of two conductive glasses, over one of which the functional layer of the electrochromic material (W-V-O) is deposited. The second conductive glass could be either bare, or an "ion storage" film could be deposited – the counter electrode. The two glasses are laminated by a polymeric electrolyte, in which small alkali ions are inserted. If a small voltage pulse is applied to the device, electrons from the conductive glass get injected into the functional layer, for an electro neutrality of the circuit, ions from the polymeric electrolyte intercalate into the film, and in result the newly formed film structure becomes absorptive, *i.e.* absorbs part of the solar light, and what we see is the complementary color. If W-V-O is the functional layer, the color we see is dark blue, because of the infrared absorption of the basic material is the tungsten oxide [1].

The electrochromic materials gained great scientific interest as they find applications in automobiles, sunroof of buildings, display devices, light regulation and architectural glazing [2]. Among various metal oxide films as electrochromic electrodes, NiO is an interesting material as it changes its color from transparent to deep brown at a positive potential, and can be reversibly bleached when the potential is reversed.

The advantages of the chemical vapor deposition at atmospheric pressure is the fact, that in a large-scale production a flow-through process is possible when the deposition goes at atmospheric pressure. CVD MoO_3, WO_3 and mixed films based on these oxides are intensively studied in our previous work [4]. Among those transition metal oxides, tungsten trioxide appears to be the best EC compound [3]. Its advantages are high coloration efficiency, good stability, and relatively low cost. However a major disadvantage of the APCVD process for WO_3 deposition is the very low growth rate. Mixing tungsten oxide with other transition metal oxide led to considerable increasing of the growth rate, and improvement of layer properties especially in optical and electrochromic aspects [4]. We relate the role of vanadium oxide (originating from $V(CO)_6$ precursor) in increasing the growth-rate, it vaporizes easier and forms growth centers, and tungsten hexacarbonyl vapors start forming the film faster. Films are much thicker at the same technological conditions compared with the single WO_3 oxide films.

Nickel oxide thin films can be used and is largely studied as functional material for transparent conductive oxide [5, 6], for application in flexible non-volatile memory devices, [7] electrochemical capacitors [8].

In this work, we present preparation and investigation of mixed W-V-O films, deposited on glass and conductive glass substrates by APCVD method. Structural properties are studied by Raman and FTIR spectroscopy. Optical characterization is performed. A brief discussion is presented, regarding the usage of NiO thin films, deposited by electrodeposition. The NiO films, exhibiting anodic coloration, in addition to the cathodic of the functional layer, are envisaged as counter electrodes in the ECD device. Electrodeposition method is relatively simple, low cost, does not require long technological time, and post treatment such as heating, etc.

2. Experimental

W-V-O thin films were obtained by atmospheric pressure CVD in oxygen ambient. The precursor used was a mixture of $W(CO)_6$ and $V(CO)_6$ in a ratio $W(CO)_6$:$V(CO)_6$ = 10:1 in a cold-wall horizontal CVD reactor. The substrate temperature was kept at 200 $^{\circ}$C. ITO coated glasses (Donnelly type) were used as substrates. The sublimator temperature was 70 $^{\circ}$C. The other important technological parameter is the ratio of the flow-rates of the carrying carbonyl vapors - Ar flow and the flow-rate of the reactive gas, oxygen (O_2). In this study, the gas flow-rates ratio was Ar/O_2 = 1/32 corresponding to 0.1 l/min/3.2 l/min. The deposition time was kept in the range 20 - 40 min. Film thickness was measured by Profilometer. The thickness of W-V-O thin films was in the range 100 - 600 nm.

NiO thin films were deposited by electrodeposition for various deposition times. The sets of samples were deposited for 20, 30, and 40 minutes, accordingly. We used an electrodeposition chamber, filled with $NiCl_2$ (0.5 M) + KCl (0.1 M) and EDTA for complexing the solution. KOH was used to adjust the pH of the solution to 8. The thickness of the NiO samples was in the range around 100 nm. NiO film deposited for 20 minutes is 119 nm thick, while the film deposited for 40 minutes is 150 nm. After annealing the film deposited for 40 minutes (annealed at $400\ ^{o}C$) decrease in thickness was observed, reaching 106 nm.

FTIR measurements were performed in the spectral range of 350-1200 cm^{-1} by Shimadzu FTIR Spectrophotometer IRPrestige-21. The studied samples were deposited on Si substrates and bare Si wafer (p-Si, with orientation <100>) was used as background. Raman spectra were also investigated. The Raman spectra were obtained using LabRAM HR Visible micro-Raman spectrometer. The 633 nm line of a He-Ne laser were used for excitation. An X50 objective was used both to focus the incident beam and to collect the scattered light in backscattering configuration. To prevent the samples by local laser overheating a low laser power (1.3 mW and 0.70 mW) was used. UV-VIS spectrophotometric study was made by UV 3600 Shimadzu spectrometer in the spectral range of 300-1000 nm.

The surface morphology of the studied metal oxide films was investigated by AFM (Atomic Force Microscope) DiMultimode V model (Veeco) in tapping mode. Scan rate was 1.5-2 Hz, the images resolution was 512 samples/line. The samples were scanned at least at two places. Silicon cantilevers (1-10 Ohm-cm Phosphorus (n) doped Si) with a resonance frequency of 250-308 kHz, force constant 20-80 N/m, tip radius < 10 nm, 50 ±10 nm Al coating on the back side (MPP-11120-10, Veecoprobes) were used in the dynamic AFM experiments. Image processing was performed by means of Nanoscope 7.30. Electrochromic characterization was performed by voltametry measurements.

3. Results and Discussion

Previous study of APCVD WO_3 – MoO_3 films shows predominantly amorphous structure of the mixed W-Mo-O films, [9] and APCVD WO_3 films grown at the same technological conditions also remain amorphous - even after high temperature annealing at $500\ ^{o}C$.
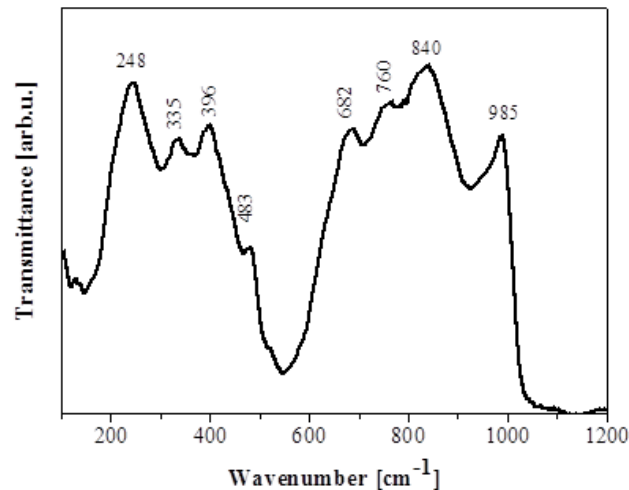

Figure. 1. Raman spectra of APCVD W-V-O films in as deposited state.

On Figure 1 are presented the Raman spectra of APCVD mixed W-V-O films in as-deposited state. The Raman band at 248 cm^{-1} is due to the deformation modes of the two possible metal oxides in the mixed oxide film structure. The band at 335 cm^{-1} is attributed to the bending vibrations of crystalline WO_3. The bands at 682 and 840 cm^{-1} correspond to the two different types of bridging oxygen of v(O-W-O) vibrations [10]. The line at 985 cm^{-1} is assigned to terminal double bonds W=O or/and V=O bonds. The vanadium oxide component is represented by two weak Raman lines at 396 and 483 cm^{-1}, which can be assigned to the bending vibrations of V-O-V and to stretching V-O bonds of orthorhombic V_2O_5 [11]. In the same time, some contribution from W-O-W stretching vibration in the absorption band 480 cm^{-1}can be observed [12].

Raman study of APCVD W-V-O films reveals that the film structure is predominantly amorphous as the observed bands are broad and with a low intensity. The amorphous structure of electrochromic film favors the intercalation and deintercalation of the small ions, and enhances the electrochromic properties.
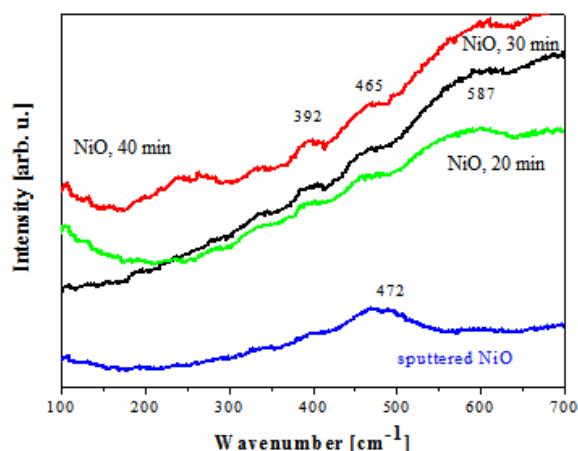

Figure. 2. Raman spectra of electrodeposited NiO_x films.

Raman spectra were measured for the NiO films, as well. Figure 2 presents the Raman spectra of electrodeposited nickel oxide samples, revealing weak and broad Raman bands. When nickel oxide is in its paramagnetic phase with rock-salt structure, no first order Raman scattering is expected [13]. However, when NiO is antiferromagnetically ordered or defect-rich, the intensity of scattering increases [13]. In general NiO films, deposited by various technologies, exhibit different microstructures and crystal phases, possess oxygen deficiency and imperfections. The peak at 392 cm^{-1} is attributed to Ni-O stretching mode of nonstoichiometric compound. Similarly, the bands located at 465 cm^{-1} (electrodeposited films) and at 472 (sputtered NiO) cm^{-1} are associated to Ni-O bonds and non-stoichiometric material [14]. The band at 587 cm^{-1} can be due to the first order longitudinal optical (LO) phonon modes of NiO. The conclusion of Raman study is that the electrodeposited NiO films are non-stoichiometric and no clear Raman lines assigned to crystalline NiO are observed.

The APCVD deposited W-V-O films were also investigated by FTIR Spectroscopy in as deposited state and after annealing at 500 °C in air for 1 hour (Figure 3). FTIR measurements for pure WO_3 films are also given as comparison. The WO_3 films are obtained under similar CVD conditions.

FTIR study shows that the spectra of mixed oxide films are very similar in shape to the corresponding spectra of pure tungsten oxide films, but the revealed absorption bands are with lower intensity. Meanwhile, several weak absorption bands were detected, that can be attributed to the vanadium oxide component.

FTIR spectra of pure tungsten oxide films show broad absorption bands. In as deposited state, there is a band spreading in the spectral range 600-732 cm^{-1}. There can be found a contribution from several deformations, and stretching modes of WO_3 [6]. After thermal treatment at 500 °C, the broad band is splitting into two strong lines at 724.0 and 801.9 cm^{-1}, similar splitting of the absorption band can be seen in the spectra of the annealed mixed oxide sample. These two IR maxima are the most characteristic for the presence of monoclinic crystalline WO_3 [7].

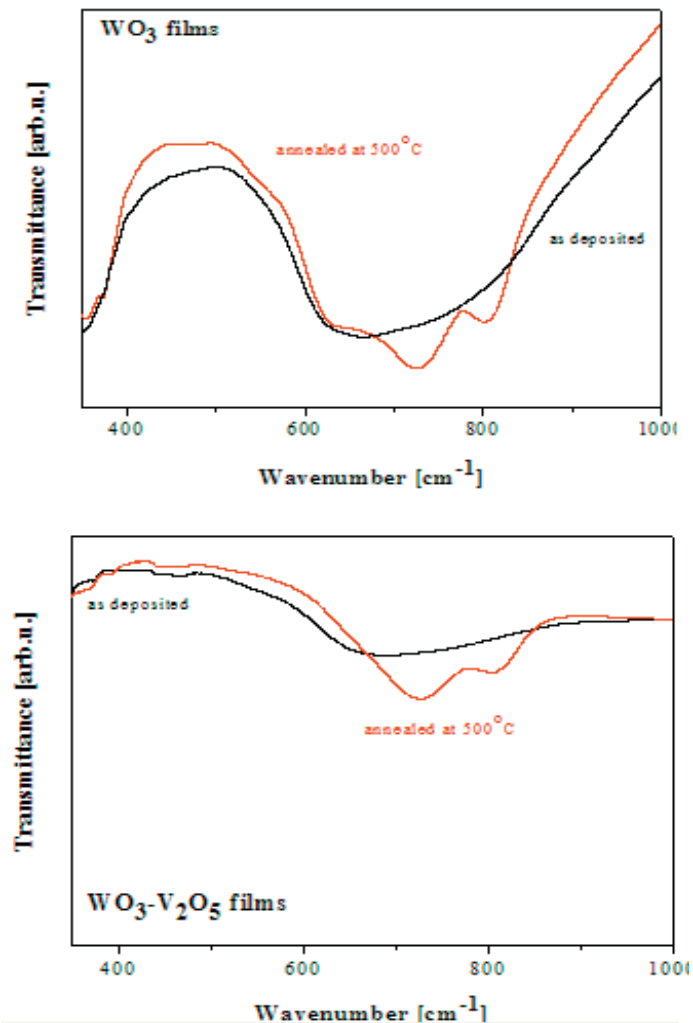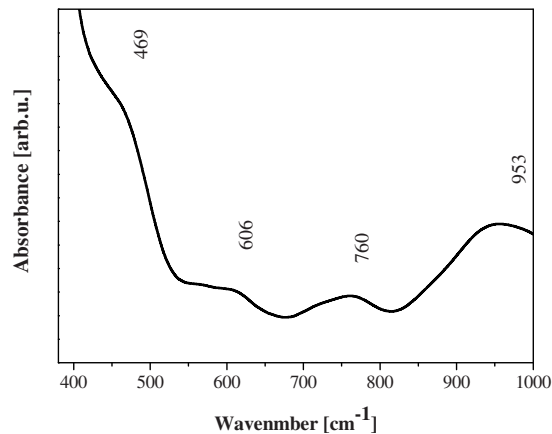Figure 3. FTIR spectra of APCVD WO_3 and W-V-O films as deposited and annealed at 500°C.

Figure 4. IR spectrum of electrodeposited NiO film, measured in reflectance mode.

In the FTIR spectra of the mixed W-V-O oxide films, the weak bands due to the stretching and bending vibrations of V-O bonding appeared in spectral range $400 – 470$ cm^{-1} [8]. In the range above 750 cm^{-1} some IR band assigned to asymmetrical stretching mode of V-O-V vibrations can be found. The FTIR study clearly indicates that although there is a small amount of vanadium carbonyl in the precursor mixture, the vanadium oxide is presented into the films structure and gives its effect on their properties.

FTIR measurements indicate bands characteristic for separate W-O and V-O bonds, which shows that the films are mixture of two phases.

NiO films were also studied by FTIR spectroscopy in reflectance mode (Figure 4). The bands appeared at 469 cm^{-1} and at 606 cm^{-1} can be assigned to the stretching vibrations of Ni-O bonds [15]. The broad absorption around 760 cm^{-1} is related to the C=O band stretching vibrations [16]. The IR band at 953 cm^{-1} can be due to the bending vibrations of OH groups. This suggestion is confirmed with weak bands detected at 3744 and at 1590 cm^{-1}, attributed to the stretching and bending modes of water incorporation [15] (this part of IR spectrum is not shown here).
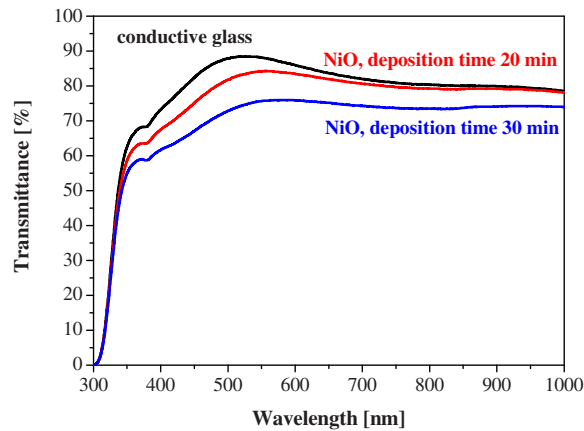
Figure 5. UV-VIS spectra of electrodeposited NiO films at different deposition times compared with bare conductive glass substrate.

Optical measurements were performed in the spectral range of 300 - 1000 nm. The electrodeposited NiO films show good transparency in the visible spectral range with high values such as 75% (550 nm) for the film deposited for 30 minutes and 85% NiO film deposited for 20 minutes (Figure 5). The films are measured without any additional thermal annealing.

APCVD W-V-O films obtained on conductive glass shows transparency around 50% in as deposited state and after thermal treatment at higher temperature, their optical behavior improves and the transmittance reaches up to 75% at 550 nm (Figure 6).

As it is seen from Figure 7, as-deposited films have smooth surfaces, some crystals are seen on the surface, probably related to a second phase rich of metallic component, non-oxidized vanadium or tungsten. When heated to 500 $^{\circ}$C the films have the typical for the mixed transition metal oxides surface, consisting of grains, which are not homogeneous and they possess probably some clustering formation. It is noticeable, that the contrast changes over the cluster grain surface, this we relate to grain boundaries. As our previous studies with W-Mo-O mixed films have shown, [4, 9] these newly formed grain boundaries would improve the ion intercalation in the working, functional film structure.
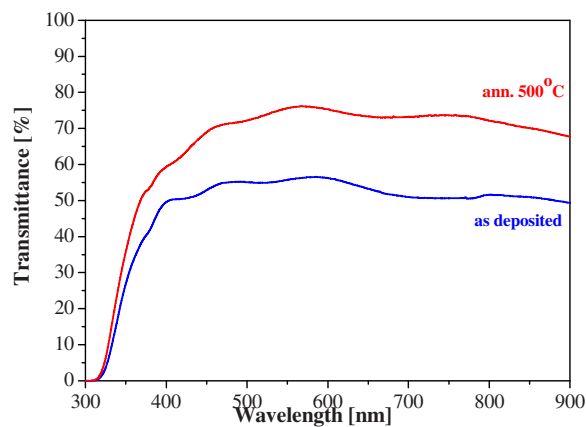

Figure 6. UV-VIS spectra of as-deposited and annealed at 500 $^{\circ}$C APCVD W-V-O films. The substrate is conductive glass.
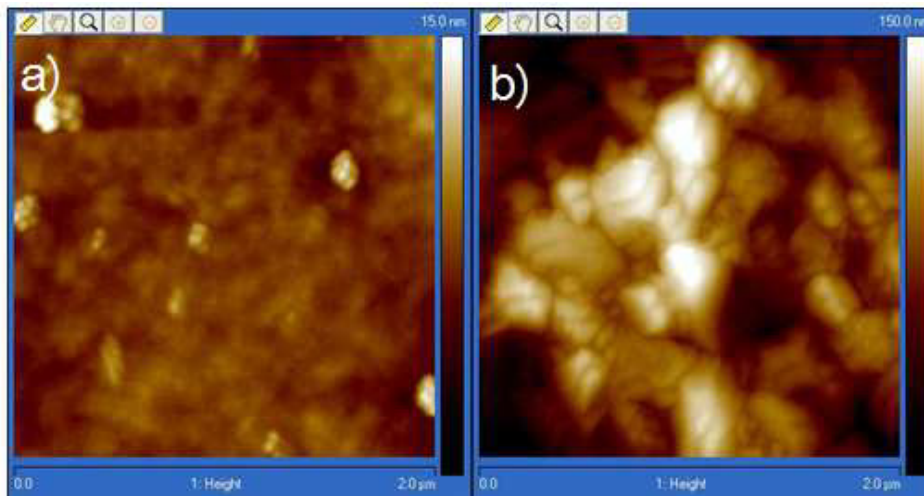
Figure 7. AFM Micrographs of as-deposited (a), and annealed at 500 $^{\circ}$C W-V-O film.

Electrochromic test was performed in a three electrode configuration, with annealed W-V-O film on conductive glass as functional electrode, electrochemically derived NiO on conductive glass as a counter electrode, and Calomel Reference Electrode, as reference electrode. The electrolyte was a 0.6 M LiClO$_4$ in Propylene carbonate (PC) placed in a quartz cuvette. Coloration was observed under a small voltage applied.

On the Figure 8 the voltamograms for as-deposited and annealed W-V-O films are presented. No significant change is observed in the behavior of the switching functional film after annealing at 500 $^{\circ}$C. Table 1, data for the color efficiency (CE) and the optical modulation is given.

The transmittance value after annealing at 500 $^{\circ}$C W-V-O films is higher than for the as-deposited films. Nevertheless, the calculated value for the color efficiency is lower, which means that the intercalated electrical charge is changed in a way that the resulting value for the CE is decreased. At the same time, the value of the optical modulation, namely the difference between the transmittance in colored and bleached state is increased from 65% up to 73-74%. Depending on the application envisaged, where either the CE or optical modulation is more important, the stage of film annealing can either be kept or removed from the overall technology of mixed W-V-O electrochromic films.
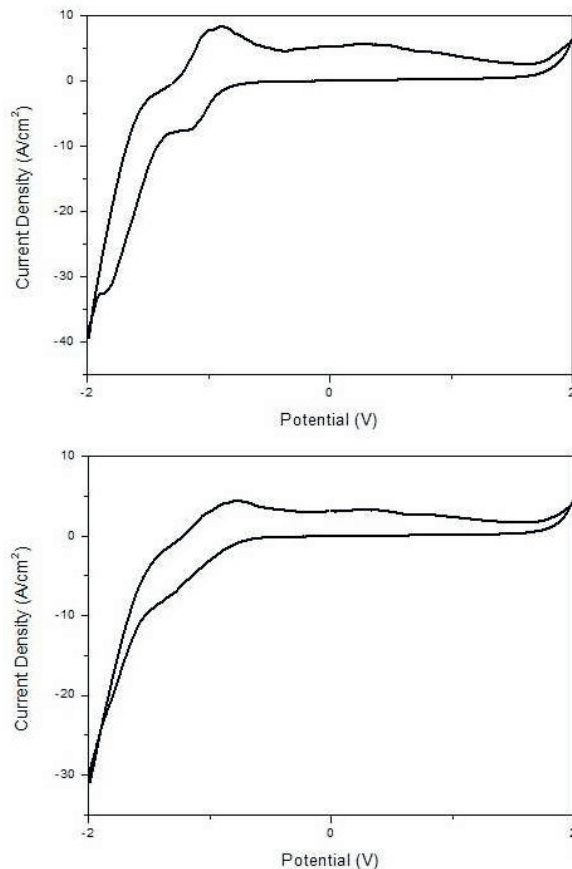
Figure 8. Voltamograms for as-deposited (top) and annealed at 500 °C (bottom) W-V-O film.

4. Conclusions

APCVD process proceeding at atmospheric pressure is developed for deposition of mixed W-V-O films to serve as functional layers in electrochromic device – "smart window". Films are deposited on conductive glass substrates, the coverage is excellent, and the growth-rate increased compare to our previously studied single APCVD WO_3 oxide films. The AFM structural investigation shows clustering, a change in the contrast of the cluster surface is observed, showing an increased area of the grain-boundaries. This is expected to facilitate intercalation of electrical charge in and out of the film structure. Developed is also an electrochemical procedure for deriving NiO film on conductive glass substrate to serve as counter electrode. Films show high transmittance which is important for the high initial transmittance of the smart window. Raman and FTIR spectra show Raman peaks and absorption bands respectively, revealing monoclinic WO_3, and orthorhombic V_2O_5 phases, separately existing in the mixed oxide film structure.

References

[1] Deb S., 1969. Appl. Opt. Suppl. 3192.

[2] Granqvist C.G., 1995. Handbook of Inorganic Electrochromic Materials, Elsevier Science, Amsterdam.

[3] Monk P. M., Mortimer R. J., Rosseinski D. R., 2007. Electrochromism and Electrochromic Devices, University Press, Cambridge.

[4] Gesheva K. A., Eds/Authors, 2007. Thin Film Optical Coatings for Effective Solar Energy Utilization: Spectrally Selective Surfaces and Energy Control Coatings, Novapublishers, New York.

[5] Reddy A. M., Reddy A. S., Reddy P. S., 2011. Vacuum 85, p. 949.

[6] Hsu C. et al., 2012. Electrochemica Acta 66, p.201.

[7] Wang H., Zou C., Zhou L., Tan C., Fu D., 2012. Microelectronics Engineering 91, p.144.

[8] Zhang Y. Q., Xia X. H., Tu J. P., Mai Y.Y., Shi S. Y., Wang X. L., Gu C. D., 2012. J. Power Sources 199, p. 413.

[9] Gesheva K. A., Ivanova T., Kozlov M., Boyadzhiev S., 2010. J. Cryst. Growth 312, p. 1188.

[10] Songara S., Kupta V., Patra M. K., Singh J., Saini L., Gowd G. S., Vadra S. R., Kumar N., 2012. J Physics Chemistry solids 73, p.851.

[11] Senthil K., Kwak G., Jong K., 2012. Applied Surface Science doi:10.1016/j.apsusc.2012.04.060.

[12] Boukriba M., Sediri F., Gharbi N., 2010. Polyhedron 29, p. 2070.

[13] Mironova-Ulmane M., Kuzmin A., Sterns I., Grabis J., Sildos I., Pars M., 2007. J. Phys.: Conference Series 93, p. 012-039.

[14] Nel J.M., Auret F. D., Wu L., Legodi M. J., Meyer W. E., Hayes M., 2004. Sensors Actuators B 100, p.270.

[15] Purushothaman N. K., Joseph Antony S., Muralidharan G., 2011. Solar Energy 85, p. 978.

[16] Qia H., Wei Z., Yang H., Zhu L., Yan X., 2009. Journal of Nanomaterials Volume 2009 Article ID 795928.