IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 10, Issue 5 Ver. II (May. 2017), PP 64-69
www.iosrjournals.org

Structural And Supercapacitive Performance Of V_2O_5 Thin Films Prepared By DC Magnetron Sputtering

G. Lakshmi Sandhya, M. Dhananjaya, N. Guru Prakash,
A. Lakshminarayana, P. Rosaiah, O. M. Hussain*
Thin films laboratory, Department of Physics, Sri Venkateswara University, Tirupati-517502, India

Abstract: *Nanocrystalline V_2O_5 thin films were deposited by dc-magnetron sputtering at various substrate temperatures keeping O_2 to Ar ratio at 1:8. The microstructural features were studied by XRD and Raman measurements while the surface topography and grain size of the films by AFM. The films deposited at 250 ˚C exhibited predominant (001) orientation representing the orthorhombic crystal structure with Pmmn space group. The observation of well resolved vanadyle mode at 993 cm^{-1} and very strong vibrational mode at 142cm^{-1} in Raman spectrum confirms the formation of layered like structure. The surface of the film is comprised of nanocrystallites with an average grain size of 32 nm and surface roughness of 14 nm. The V_2O_5 thin films deposited on Ni substrates exhibited good electrochemical performance with high specific capacitance of 238 F/g current density of 1 $mAcm^{-2}$ with good cycling stability.*

Keywords: *V_2O_5 thin films, DC-magnetron sputtering, electrochemical properties.*

* *Corresponding Author e-mail: hussainsvu@gmail.com*

I. Introduction

The development of energy storage and conversion devices associated with suitable and novel technologies have much attracted now a days. Batteries, supercapacitors, and conventional capacitors are commonly used as energy storage devices [1]. Supercapacitors or electrochemical capacitors are a subclass of energy storage devices, which utilize electrical double layer phenomena to store energy. As supercapacitors store energy on the surface of the active material, the charging-discharging occurs at faster rates which results in high power densities and high cycling stability. In addition, Supercapacitors have the advantages of long cycle life, high power density, wide working temperature range, and environmental friendliness [2, 3]. Typically supercapacitors are characterized into two classes viz. electrochemical double layer capacitor (EDLC), which is based on non-faradic charge storage and pseudocapacitors wherein charge transfer is brought about by virtue of faradic electrochemical redox reactions undergone by specific electrochemically active elements within a compound [4]. With regards to the systems providing high power and energy densities, pseudocapacitors are more suitable on account of the charge storage mechanism that tends to be a hybrid match of both the battery and supercapacitor worlds. In this perception, the study and investigation of electrode materials for pseudocapacitors are very important in order to compete with batteries. The electrochemical performance of the active electrode materials plays an important role in the construction of a supercapacitor.

Transition metal oxides have much attracted due to variable properties with multiple oxidation states [5-8]. Among various transition metal oxide materials, V_2O_5 has been considered as one of the most promising and persistence material in terms of its broad oxidation states, low cost, non-toxic nature, natural abundance and also high theoretical capacitance (294 $mAhg^{-1}$). V_2O_5 has orthorhombic layered structure, in which the vanadium atom present in pentavalent state having V-O bonding with the lattice parameters a = 1.15 nm, b = 0.35 nm and c = 0.436 nm, which helps to participate more Li-ions in electrochemical redox reactions [9, 10]. Moreover, vanadium pentoxide is the most stable phase among all magneli phases (V_nO_{2n+1}), exhibits interesting electrical, optical and electrochemical properties [11].

V_2O_5 thin films can be prepared by a wide variety of physical and chemical deposition methods such as sputtering [12, 13], thermal evaporation [14], pulsed laser deposition [15, 16], atomic layer deposition [17], Sol-Gel [18], dip coating [19], spray pyrolysis [20] etc. Among various plasma assisted thin film deposition techniques, the dc magnetron sputtering method has been recognized as one of the very simple, versatile and pioneered technique to grow V_2O_5 thin films with desirable stoichiometry and excellent adhesion with good uniformity [21]. In addition, the reaction occurs predominantly in plasma region resulting to control the chemical composition of the films by properly controlling the ratio of reaction species. In particular, the deposition parameters such as the partial pressure of sputtering gas (O_2 and Ar), substrate temperature and annealing temperature play very important role in controlling the microstructure of thin films. In particular, the substrate temperature plays an important role during the preparation of thin films since, the relaxation time to dissipate kinetic energy of sputtered species, surface diffusion and surface structural changes are thermally

activated processes. Further, the optimization of substrate temperature is of great importance in preparation of thin films as it directly related to the phase changes induced in vanadium oxides and also causes noticeable changes in microstructural, electrical, optical, electrochemical properties of vanadium oxide thin films. Therefore in the present work, V_2O_5 thin films are prepared by dc magnetron sputtering. The microstructural properties of films are studied as a function of varying substrate temperature, maintaining O_2 to Ar ratio constant at 1:8 and DC power was 500 W. Finally, good electrochemical performance was reported for the vanadium pentoxide thin film electrodes deposited at 250 ˚C.

II. Experimental

Vanadium pentoxide (V_2O_5) thin films were deposited from a three-inch vanadium metal target of 99.99 % purity using DC magnetron sputtering technique onto well cleaned nickel and glass substrates. The distance between the target and the substrates was maintained constant at 55 mm. The film growth was performed in O_2 /Ar atmosphere with a constant composition ratio at 1:8 and the substrate temperature (T_S) was varied from 30 ˚C to 350 ˚C. The DC power maintained during sputtering was 500 W, and the pressure inside the chamber while in the process of sputtering was about 8.0 $x10^{-3}$ mbar.

The structure of the grown vanadium pentoxide thin films was studied by Seifert X-ray diffractometer with $CuK_{\alpha 1}$ radiation (λ = 0.15406 nm) in the 2θ range from 10˚ to 70˚ with the step width of 0.04˚/s. The peak positions were determined precisely using RAYFLEX- Analyze software, and the lattice parameters were calculated by using the standard formula. The surface morphological studies were carried out by NT-MDT SOLVER NEXT Atomic Force Microscope (AFM). The Optical transmittance of the prepared thin films were recorded over the wavelength range from 350-850 nm using Perkin Elmer Lambda 950-UV-Vis-NIR double beam spectrometer.

The electrochemical properties of vanadium oxide thin films were investigated using a three-electrode cell with V_2O_5 thin films coated on Ni-substrate as working electrode, platinum strip wire as a counter electrode and Ag/AgCl as reference electrode and 1M Li_2SO_4 solution as electrolyte. The electrochemical properties were carried out using a CHI 608C electrochemical analyzer instrument.

III. Results and Discussion

Microstructural Properties

The XRD patterns of as deposited vanadium pentoxide thin films on Ni substrates at various substrate temperatures (Ts) are shown in Fig.1. The X-ray diffraction patterns of V_2O_5 thin films deposited at substrate temperatures less than 150 ˚C did not reveal any characteristic features indicating that the films are amorphous in nature. The films were found to be transparent pale yellow in color and readily dissolved in water yielding a clear yellow solution which confirms the amorphous nature of the films as suggested by Livage et al [24].

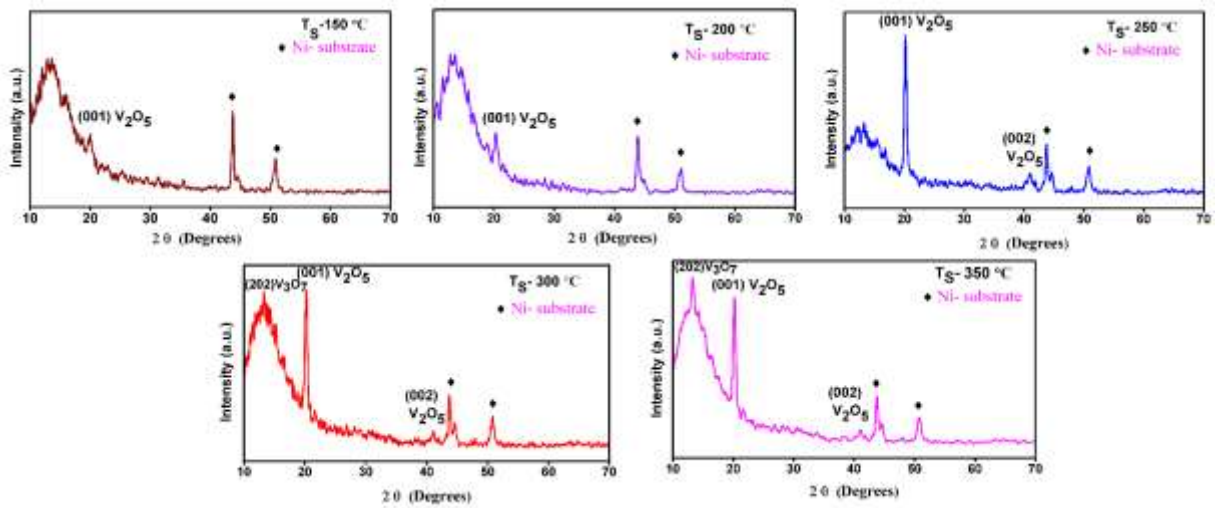

Figure 1. XRD Spectra of as deposited vanadium pentoxide thin films on Ni substrates at various temperatures

The Bragg reflection corresponds to (001) orientation has been observed for the films deposited at Ts =150 ˚C indicating that the onset crystallization has been initiated. The films deposited at higher substrate temperatures exhibited predominant (001) orientation along with other characteristic orientations such as (200), (101), (110), (002) and (004) indicating that the growth is along the crystallographic z-axis. As the substrate temperature increased to 300 ˚C, the (202) reflection corresponds to V_3O_7 phase appeared at 13.20˚ and the intensity of (001) diffraction peak reduced indicating the presence of mixed phases. Furthermore the additional impurity peaks at

high temperature (> 250 ˚C) may be due to oxygen deficiency [25]. The films deposited at 250 ˚C crystallized as pure V_2O_5 phase. The average crystalline size of the films is calculated using the Scherrer's equation. The calculated crystallite sizes of V_2O_5 films deposited at 250, 300 and 350 ˚C are 22 nm, 35 nm and 46 nm, respectively. By increasing the substrate temperature, the mobility of the adatoms increases then diffusion takes place on the substrate surface which result an enhancement in the crystallite size. Moreover, the low crystallite size of thin films provide high surface-to-volume ratio, which causes shorten charge transfer distance, suppress irreversible phase transition and lead to significant improvement of cycling stability, storage capacity and electrochemical kinetics. The lattice parameters of the films deposited at 250 ˚C are a = 1.151 nm, b = 0.354 nm and c = 0.437 nm, which are in good agreement with the reported values [26-30].

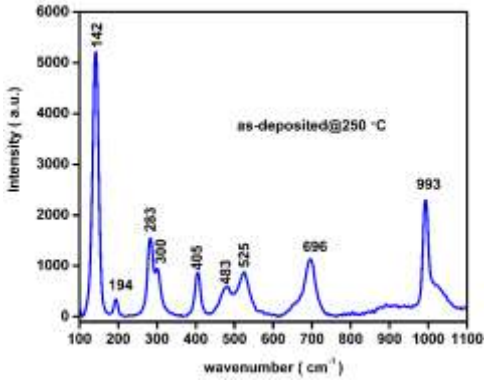

Figure 2. Raman spectrum of V_2O_5 thin films deposited at 250 ˚C

Fig.2 shows the Raman spectrum of V_2O_5 thin films deposited at 250 ˚C in the wavelength range of 100-1200 cm^{-1}. The spectrum exhibited highly resolved Raman peaks correspond to internal and external modes, indicative of the high purity films. The stretching and bending V-O bonds correspond to internal modes which are located at high frequency region, while external modes located at low frequency region. The high intense peak at 142 cm^{-1} corresponds to the vibrations of O-V-O-V-O and is direct evidence of layered structure of V_2O_5. The peaks at 283 and 405 cm^{-1} assigned to V=O bending vibration, while the peak at 485 cm^{-1} to the bending vibration of the bridging V-O-V bonds. A peak at 525 cm^{-1} is ascribed to the stretching mode of V-O, resulting from edge-shared oxygen. A peak at 696 cm^{-1} is corresponds to stretching mode of V-O, which comes from the corner shared oxygen. Finally, a peak at around 993 cm^{-1} corresponds to the vanadyl terminal oxygen stretching mode, which is resultant of unshared oxygen. These results are in good agreement with Raman data reported for V_2O_5 in the literatures [24].

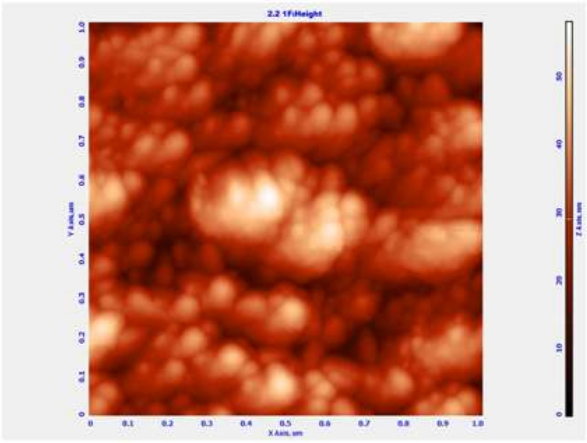

Figure 3. AFM of V_2O_5 Thin films deposited at 250 ˚C

The surface topography of as deposited V_2O_5 thin films at Ts = 250 ˚C was studied using AFM and is shown in Fig. 3. The surface microstructure data demonstrate that the film surface is composed of roughly spherical grains of various sizes. The average estimated grain size is 32 nm. The root mean square surface roughness derived from AFM data is 14 nm. The optical transmittance spectrum recorded in the wavelength region 350 - 850 nm of as deposited V_2O_5 thin films on glass substrates at Ts = 250 ˚C is shown in Fig.4. The transmission spectra of the films showed a relatively sharp absorption edge near 500 nm with a relative high percentage of transmission. The optical absorption coefficient determined from the measured transmittance spectrum for grown vanadium oxide thin films showed a better fit when $(\alpha\ h\nu)^{2/3}$ vs $h\nu$ were plotted revealing

direct forbidden optical band gap. The evaluated optical band gap was 2.42 eV which is in good agreement with the reported value for nanocrystallineV_2O_5 thin films [27].

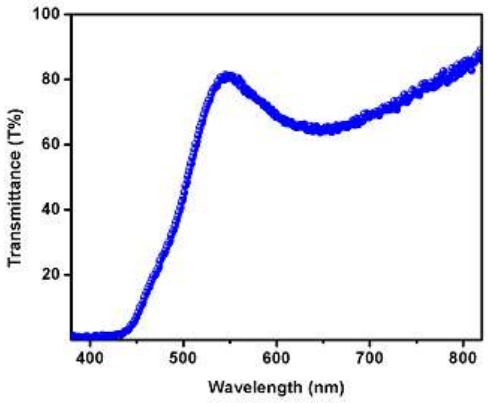

Figure 4. Transmittance spectra of V_2O_5 thin films deposited at 250 ˚C

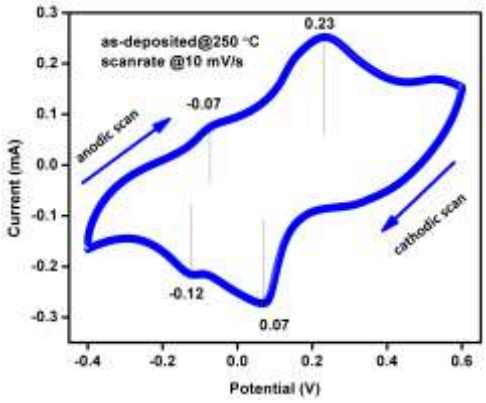

Figure 5. Cyclic voltammetry curves of V_2O_5 thin films deposited at 250 ˚C

Electrochemical Properties:

The electrochemical performance of V_2O_5 films was investigated using cyclic volammetry (CV). A three electrode cell was constructed with V_2O_5 films coated on Ni-substrate as working electrode, platinum strip as a counter electrode and Ag/AgCl as reference electrode and 1M Li_2SO_4 saturated solution as electrolyte. Fig. 5 shows the cyclic voltammogramme of as deposited films recorded in the potential window -0.4 V to 0.6 V at a scan rate of 10 mV/s. The CV of the films exhibited two distinct pairs of redox peaks located at 0.07/0.23 V and -0.12/-0.07 V respectively, which are evidently due to the Li^+ intercalation/de-intercalation reactions, accompanying gain and loss of electrons. These peaks have been attributed to two successive electrochemical process [5, 22, 23].

$$V_2O_5 + \tfrac{1}{2}\,Li^+ + \tfrac{1}{2}\,e^- \rightleftharpoons Li_{0.5}V_2O_5 \qquad \text{---------- (1)}$$

$$Li_{0.5}V_2O_5 + \tfrac{1}{2}\,Li^+ + \tfrac{1}{2}\,e^- \rightleftharpoons LiV_2O_5 \qquad \text{---------- (2)}$$

In the first reduction peak at 0.07V, only a fraction of the V^{5+} ions were reduced to V^{4+} ions and the remaining V^{5+} ions were reduced to V^{4+} ions in the second peak at -0.12 V respectively. The two anodic peaks appear at -0.07 and 0.23 V corresponding to the lithium de-intercalation and the opposite phase transformation to the cathodic reaction. The electrochemical reactions suggests that different phases of $Li_xV_2O_5$ are formed means that the first lithium ion into V_2O_5 contributes the phase transformation from α- V_2O_5 to ε- V_2O_5 and ε- V_2O_5 to δ- V_2O_5 at 0.07 and -0.12 V respectively [16]. Reduced peak separation indicates more facile mass transport through both electrolyte and nano structured electrode with enhanced Li^+ diffusion showing improved electrochemical kinetics in V_2O_5 thin films prepared at 1:8 ratio of O_2/Ar sputtered gas with T_S = 250 ˚C.

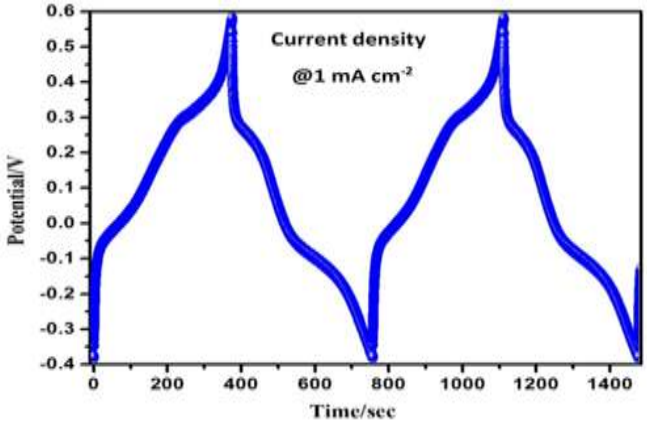

Figure 6 CP curves of V_2O_5 thin films deposited at 250 ˚C

The galvanostatic charge-discharge (GCD) studies were also carried out to understand the electrochemical performance of V_2O_5 thin films. Fig.6 shows the charge-discharge curves of optimized film electrode under a current density of 1 $mAcm^{-2}$ and in the potential range from -0.4 to +0.6 V vs Ag/AgCl. The CP curves of the film possess a more staircase-type shape, and also retain of curves indicates well defined phase transitions during intercalation and de-intercalation process. The specific capacitance (CS) of the thin films were calculated by using the formula

$$C_S = \frac{I\,dt}{m\,dV} \quad \text{(F/g)} \quad \text{..... (2)}$$

where dt–time interval and dV–potential difference, I- current, and m- mass of the thin film. The measured specific capacitance value of film electrode was 238 F/g at current density of 1 $mAcm^{-2}$.

The electrochemical impedance spectroscopy (EIS) is one of the good techniques for the study of electrochemical properties of the prepared V_2O_5 thin films. The EIS measurements of grown thin films were measured in the frequency range from 0.1 Hz to 1 MHz and the corresponding Nyquist plot is shown in Figure.7. The impedance spectra of the thin film electrode exhibited depressed arc in high frequency region followed by a straight line with increasing the phase angle in the low frequency range. The estimated charge transfer resistance is 10 Ω. The cycling stability of V_2O_5 thin film electrode is shown in Fig. 8. The films retained 85% of its initial capacity even after 100 cycles. The V_2O_5 thin film electrode exhibited high electrochemical activity for energy storage due to its high surface area and low crystallite size without impurity phases [20, 21].

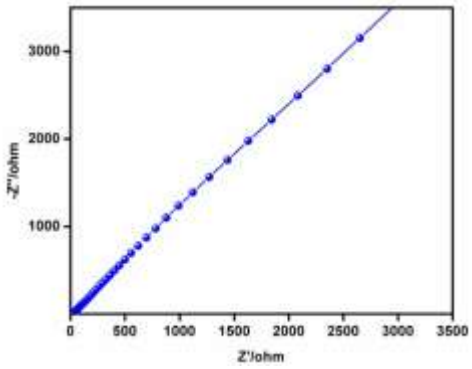

Figure 7. Nyquist plot of V_2O_5 thin films

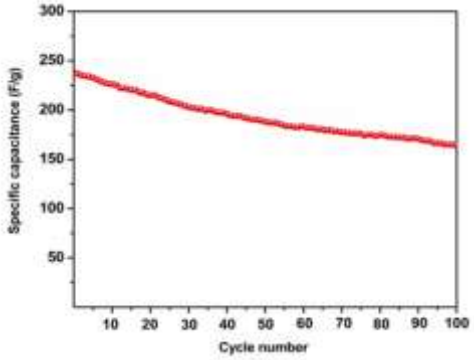

Figure 8. Cycling stability of V_2O_5 thinfilms

IV. Conclusion

Thin films of V_2O_5 were successfully prepared by dc-magnetron sputtering technique on Ni and glass substrates keeping O_2 to Ar ratio at 1:8. The films were deposited at various substrate temperatures ranging from 30 ˚C to 350 ˚C. The films deposited at 250 ˚C exhibited orthorhombic crystal structure with Pmmn space group and the estimated crystallite size and lattice parameters are 22 nm and a = 1.151 nm, b = 0.354 nm and c = 0.437 nm respectively. The surface of the films is composed of roughly spherical grains with average grain size of about 32 nm and rms surface roughness of 14 nm. The observation of well resolved vanadyl mode at 993 cm^{-1} and very strong vibrational mode at 142 cm^{-1} in Raman spectrum confirms the formation of layered like structure. The CV, GCD and EIS measurements were performed to understand the supercapacitive behavior of the V_2O_5 film electrode deposited on Ni substrates by constructing an electrochemical cell. The films exhibited good electrochemical performance with high specific capacitance of 238 F/g at a current density of 1 $mAcm^{-2}$ with good cycling stability.

References

[1]. B.Purusottam Reddy, K. Sivajee Ganesh, O. M. Hussain, Growth, microstructure and supercapacitive performance of copper oxide thin films prepared by RF magnetron sputtering, Applied Physics A, 122 (2016) 128-137.

[2]. Wei Tang , Yusong Zhu, Yuyang Hou, Lili Liu, Yuping Wu, Kian Ping Loh, Hanping Zhang and Kai Zhu, Aqueous rechargeable lithium batteries as an energy storage system of superfast charging, Energy Environ, Sci., 6 (2013) 2093-2104.

[3]. Minghao Yu, Teng Zhai, Xihong Lu, Xiaojun Chen, Shilei Xie, Wei Li, Chaolun Liang, Wenxia Zhao, Liping Zhang, Yexiang Tong, Manganese dioxide nanorod arrays on carbon fabric for flexible solidstate supercapacitors, Journal of Power Sources, 239 (2013) 64-71.

[4]. Zhitong Li, Guoxue Liu, Min Guo, Liang-Xin Ding, Suqing Wang, Electrospun porous vanadium pentoxide nanotubes as a high-performance cathode material for lithium-ion batteries, Electrochimica Acta, 173 (2015) 131-138.

[5]. Huanqiao Song, Cuiping Zhang, Yaguang Liu, Chaofeng Liu, Xihui Nan, Guozhong Cao Facile synthesis of mesoporous V_2O_5 nanosheets with superior rate capability and excellent cycling stability for lithium ion batteries, Journal of Power Sources, 294 (2015) 1-7.

[6]. M.Nazemiyan and Y. S. Jalili, Record low temperature Mo doped V_2O_5 thermochromic thin films for optoelectronic Applications, AIP Advances, 3 (2013) 112103(1-7).

[7]. Y.S. Yoon, J.S. Kim, S.H. Choi, Structural and electrochemical properties of vanadium oxide thin films grown by d.c. and r.f. reactive sputtering at room temperature, Thin Solid Films, 460 (2004) 41-47.

[8]. Marcelo S.B. de Castro, Carlos L. Ferreira, Roberto R. de Avillez, Vanadium oxide thin films produced by magnetron sputtering from a V_2O_5 target at room temperature, Infrared Physics & Technology, 60 (2013) 103-107.

[9]. Jhih-Syuan Ke, Sheng-Feng Weng, Ming-Cheng Wu, Chi-Shen Lee, Controlled synthesis of VO_2(R), VO_2(B), and V_2O_3vanadium-oxide nanowires, J. Nanoparticle Res., 15 (2013) 1632(1-9).

[10]. Guangming Wu, Kaifang Du, Changsheng Xia, Xiao Kun, Jun Shen, Bin Zhou, Jue Wang, Optical absorption edge evolution of vanadium pentoxide films during lithium intercalation, Thin Solid Films, 485 (2005) 284-289.

[11]. C.V. Ramana, R. J. Smith, O. M. Hussain, M. Massot and C. M. Julien, Surface analysis of pulsed laser-deposited V_2O_5 thin films and their lithium intercalated products studied by Raman spectroscopy, Surface and Interface Analysis, 37 (2005) 406-411.

[12]. Trilok Singh, Shuangzhou Wang, Nabeel Aslam, Hehe Zhang, Susanne Hoffmann-Eifert, and Sanjay Mathur, Atomic Layer Deposition of Transparent VOxThin Films for Resistive Switching Applications, Chem. Vap. Deposition, 20 (2014) 291-297.

[13]. Fatma Pinar Gökdemi,Ayse Evrim Saatci, Orhan Özdemir, and Kubilay Kutlu, Structural Modification of Sol-Gel Synthesized V_2O_5 and TiO_2 Thin Films with/without Erbium Doping , Advances in Materials Science and Engineering, Volume 2014, Article ID 795384, 8 pages.

[14]. Yuanzhi Li, Toyoki Kunitake, and Yoshitaka Aoki, Synthesis and Li+ Intercalation/Extraction in Ultrathin V_2O_5 Layer and Freestanding V_2O_5/Pt/PVA Multilayer Films, Chem. Mater., 19 (2007) 575-580.

[15]. C E Patil, N L Tarwal, P S Shinde, H P Deshmukh and P S Patil, Synthesis of electrochromic vanadium oxide by pulsed spray pyrolysis technique and its properties, J. Phys. D: Appl. Phys., 42 (2009) 025404 (7pp).

[16]. Ying Wang, Guozhong Cao, Li+-intercalation electrochemical/electrochromic properties of vanadium pentoxide films by sol electrophoretic deposition, Electrochimica Acta, 51 (2006) 4865-4872.

[17]. X. J Wang, H.D. Li, Y.J. Fei, X. Wang, Y.Y. Xiong, Y.X. Nie, K.A. Feng, XRD and Raman study of vanadium oxide thin films deposited on fused silica substrates by RF magnetron sputtering, Applied Surface Science, 177 (2001) 8-14.

[18]. Yuanzhi Li, Toyoki Kunitake, and Yoshitaka Aoki, Synthesis and Li+ Intercalation/Extraction in Ultrathin V_2O_5 Layer and Freestanding V_2O_5/Pt/PVA Multilayer Films, Chem. Mater., 19 (2007) 575-580.

[19]. C.V. Ramana, R. J. Smith, O. M. Hussain, C. C. Chusuei and C. M. Julien, Correlation between Growth Conditions, Microstructure, and Optical Properties in Pulsed-Laser-Deposited V_2O_5 Thin Films, Chem. Mater., 14 (2005) 1213-1219.

[20]. Aiping Jin, Wen Chen, Quanyao Zhu, Zelang Jian, Multi-electrochromism behavior and electrochromic mechanism of electrodeposited molybdenum doped vanadium pentoxide films, Electrochimica Acta, 55 (2010) 6408-6414.

[21]. Jixin Zhu, Liujun Cao, Yingsi Wu, Yongji Gong, Zheng Liu, Harry E. Hoster, Yunhuai Zhang, Shengtao Zhang, Shubin Yang, Qingyu Yan, Pulickel M. Ajayan, and Robert Vajtai, Building 3D Structures of Vanadium Pentoxide Nanosheets and Application as Electrodes in Supercapacitors, Nano Lett., 13 (2013) 5408-5413.

[22]. An-Min Cao, Jin-Song Hu, Han-Pu Liang, and Li-Jun Wan, Angew. Self-Assembled Vanadium Pentoxide (V_2O_5) Hollow Microspheres from Nanorods and Their Application in Lithium-Ion Batteries, Chem. Int. Ed., 44 (2005) 4391-4395.

[23]. Haihong Yin, Changqing Song, Yang Wang, Shouchuan Li, Min Zeng, Zhengli Zhang, Ziqiang Zhu, Ke Yu, Influence of morphologies and pseudocapacitive contributions for charge storage in V_2O_5 micro/nano-structures, Electrochimica Acta, 111 (2013) 762-770.

[24]. K. Hari Krishna, O.M. Hussain , Tailoring of electrochemical properties of V_2O_5 thin films grown n flexible substrates using plasma assisted activated reactive evaporation , Ionics, 19 (2013) 1359–1365.

[25]. C.V. Ramana, R.J.Smith O.M. Hussain, C.M. Julien, Growth and surface characterization of V_2O_5 thin films made by pulsed-laser deposition, J. Vac. Sci. Technol. A, 22 (2004) 2453-2458.

[26]. K.V. Madhuri, K. S. Rao, B.S. Naidu, O.M. Hussain and R. Pinto, Characterization of laser ablated V_2O_5 thin films, Journal of Materials Science: Materials in Electronics, 13 (2002) 425-432.

[27]. Ramis Mustafa Öksüzoğlu, Pinar Bilgic, Mustafa Yildirim and Okan Deniz , Influence of post-annealing on electrical, structural and optical properties of vanadium oxide thin films, Optics and Laser Technology 48 (2013) 102-109.

[28]. Nicholas Fieldhous, Sean M Pursel, Mark W Horn and S S N Bharadwaja, Electrical properties of vanadium oxide thin films for bolometer applications: processed by pulse dc sputtering, J. Phys. D: Appl. Phys., 42 (2009) 055408-055413.

[29]. S S N Bharadwaja, C. Venkatasubramanian, N. Fieldhouse, S. Ashok, M. W. Horn, and T.N. Jackson , Low temperature charge carrier hopping transport mechanism in vanadium oxide thin films grown using pulsed dc sputtering, Applied Physics Letters, 94 (2009) 222110 (1-4).

[30]. Congcong Zhu, Jie Shu, Xianzong Wu, Peng Li and Xing Li , Electrospun V_2O_5 micro/nanorods as cathode materials for lithium ion battery, Journal of Electroanalytical Chemistry, 759 (2015) 184-189.