Journal of Materials Science and Engineering A 6 (3-4) (2016) 81-87
doi: 10.17265/2161-6213/2016.3-4.007

# $V_2O_5$ Thin Films Deposited by RF Magnetron Sputtering: The Influence of Oxygen Content in Physical Properties

Dwight Acosta*, Argelia Pérez, Carlos Magaña and Francisco Hernández
*Instituto de Física, Universidad Nacional Autónoma de México, A.P. 20 364, 01000, Ciudad de México, MEXICO*

**Abstract:** Vanadium Oxide thin films were deposited by RF Magnetron sputtering using a $V_2O_5$ target on glass and on FTO/Glass substrates without $O_2$ and with a $O_2$ atmosphere in the deposition chamber respectively. The effects of $O_2$ on compositional, structural, electrical and optical properties has been studied using, EDS (Energy dispersive spectroscopy), XRD (X-rays diffraction), Scanning and Transmission Electron Microscopy (SEM) and (TEM) respectively, UV and Visible Spectroscopy and the Four Points method to study electric surface properties. Abrupt variations in electrical resistivity as the films were heated around 255 ºC suggest a change of phase from semiconductor to a metallic material. The β-$V_2O_5$ films present electrochromic behavior under an external voltage, but Cyclic Voltammetry experiments reveal poor durabilitty of electrochromic properties.

**Key words:** Vanadium oxide, oxygen content, thin films.

## 1. Introduction

Vanadium oxide is a material that shows a phase transition of semiconductor to metal when is heated around of a critical temperature. For the $V_2O_5$ compound, this phase transition occur at 257 ± 5 °C. The study of vanadium compounds in thin film configuration, has received special attention in recent times because of their interesting electrochromic and thermochromic properties and potential uses as thermal sensing, optical switches, optoelectronic devices and energy saving devices with emphasis in the development of smart windows [1]. $V_2O_5$ thin films have been prepared by various methods such as sputtering [2, 3], vacuum evaporation [4, 5], sol-gel [6], pulsed laser deposition [7], chemical vapor deposition[8], electron beam evaporation [9], thermal evaporation [10] and spraypyrolysis [11, 12].They have been processed in thin film configuration to develop electrical and optical devices; especially the vanadium pentaoxide ($V_2O_5$), a wide band gap and n-type semiconductor material, which is widely investigated because of its interesting thermochromic [13, 14] and electrochromic properties [15, 16].

*Corresponding author: Dwight Acosta, Ph.D., research fields: transparent conductive materials, electron microscopy characterization of materials, Synthesis and evaluation of ecomaterials.

## 2. Experimental

Vanadium pentaoxide ($V_2O_5$) thin films were deposited by RF magnetron sputtering with two deposition conditions: with and without $O_2$, using a $V_2O_5$ target. The thin films deposition was carried out using a 5 cm diameter and 3 mm thick target 99.95% pure vanadium pentoxide target (Goodfellow). The substrates were placed 50 mm in front of the magnetron and not heating was applied during the deposition. Sputtering deposition was carried out with a power of 100 W for 15 min, in a controlled Ar/$O_2$ atmosphere with an oxygen concentration of 10% at room temperature. The base pressure in the chamber was $10^{-6}$ torr and the working pressure was $10^{-3}$ torr. The $V_2O_5$ thin films were deposited simultaneously on corning glass substrates with and without conductive layer of fluorine doped tin oxide ($SnO_2$:F or FTO), with a sheet resistance of 7 ohm/sq. The $V_2O_5$ films' thickness was determined with an optical profilometer and from cross section SEM (Scanning electron microscopy) micrographs. The pristine vanadium

pentoxide films present a yellow uniform color similar to those prepared by other techniques [17].

In order to measure the optical and electrical properties of as-deposited films, different bits of the same sample were heated in an oven under the same conditions, that is, at the same heating rate and at atmospheric pressure. The temperatures reached by the oven were 100, 200, 300, 400 and 500 ºC respectively. The electrical performance of just mentioned samples was determined by means of the Jandel Multi Height Microposition probe equipment, using the four-points method. The XRD characterization was carried out using a Bruker D-8 Advance diffractometer with the Bragg-Brentano θ-θ geometry and $CuK_\alpha$ radiation. The diffraction intensity as a function of the angle 2θ was measured between $8^\circ$ and $90^\circ$, with steps of $0.030^\circ$ and a measurement time of 35.2 s per point. The Scanning Electron Microscopy observations were performed in a LV JEOL SEM 5600 microscope and Conventional and High Resolution Electron Microscopy (CTEM and HREM respectively) were performed in a JEOL FEG STEM 2010 microscope. Compositional characteristics were obtained in an EDS NORAN equipment in the scanning electron microscope.

## 3. Results

### *3.1 Structural Characterization*

The XRD pattern displayed in Fig. 1, comes from a film prepared with a 10% $O_2$ concentration and deposited at RT, present diffraction peaks reported in card number 00-045-1074 (I) from the JCP2.2CA data base. The compound is identified as the β-$V_2O_5$ phase with tetragonal structure and lattice parameters a = 14.259 Å, b = 14.259 Å and c = 12.576 Å. Low intensity diffraction peaks, not presented in this work, that might correspond to a $VO_2$, were observed in some other XRD (X-rays diffraction) patterns of our samples.

The thickness of films reported in this work were determined by Optical Profilometry and cross sectiom SEM micrographs measurements; It was found an average thickness of 380 nm for FTO and 440 nm for $V_2O_5$ films respectively.

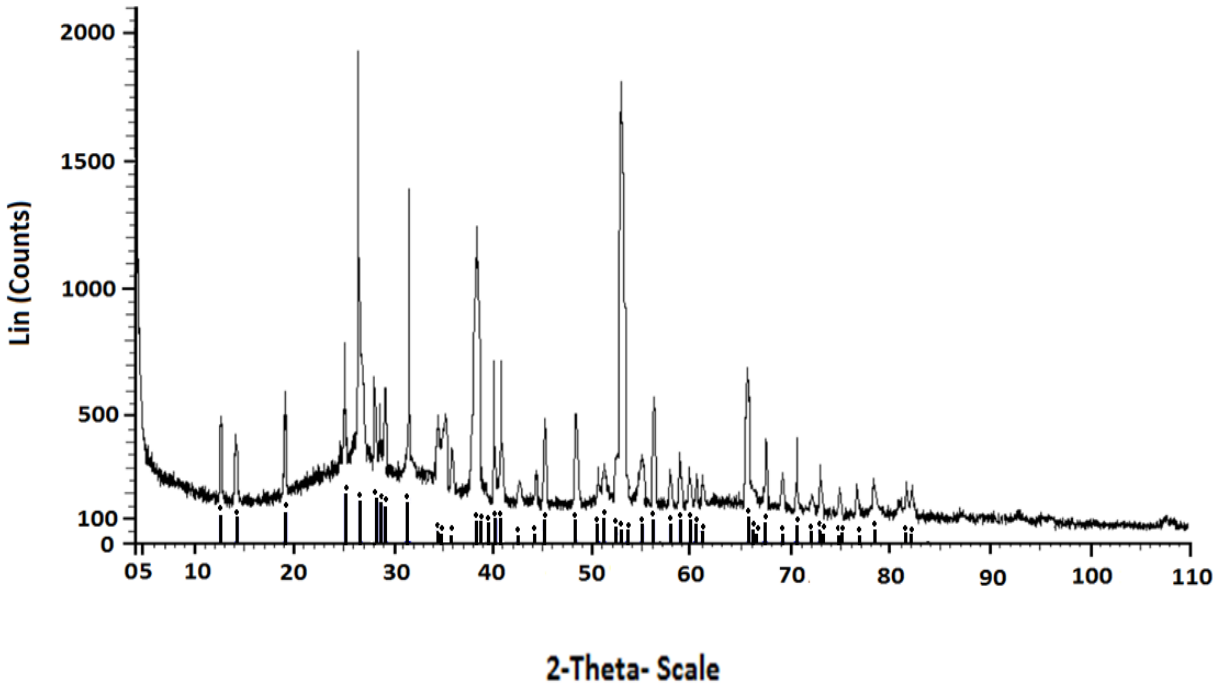



**Fig. 1 A XRD pattern from a $V_2O_5$/FTO film deposited at room temperature. The peaks marked with blue short lines correspond to the β-$V_2O_5$ reflections reported in card number 00-045-1074 (I) from the JCP2.2CA data base.**

*3.2 Composition*

The compositional properties of pristine $V_2O_5$ films, were studied by EDS (Energy dispersive spectroscopy) in a scanning electron microscope. In Fig. 2a, a typical EDS spectrum of a pristine sample is presented together with compositional results displayed in inserted Table I. In Fig. 2b an EDS spectra of a $V_2O_5$ sample, similar to the one presented in Fig. 2a, but after 60 cycles of cyclic voltammetry is displayed together with the corresponding results displayed in Table II. A comparison from quantification presented tables I and II respectively, let to detect a noticeable diminishing vanadium content in the pristine $V_2O_5$ samples. XPS compositional results are displayed in Fig. 3, it can be noticed the presence of signals corresponding to $VO_2$ and $V_2O_5$ compounds in both the films synthesized with and without $O_2$ in the deposition chamber.

*3.3 Electron Microscopy*

From the bright field TEM micrograph displayed in Fig. 3a, it can be appreciated laminates of vanadium oxide film growth on a FTO substrate. Fig. 3b is a HREM micrograph, where typical configuration of our films, can be appreciated: a polycrystalline nature of vanadium oxide grains together with amorphous zones. The structural surface details of $V_2O_5$ films can be appreciated in SEM micrographs presented in Fig. 5.

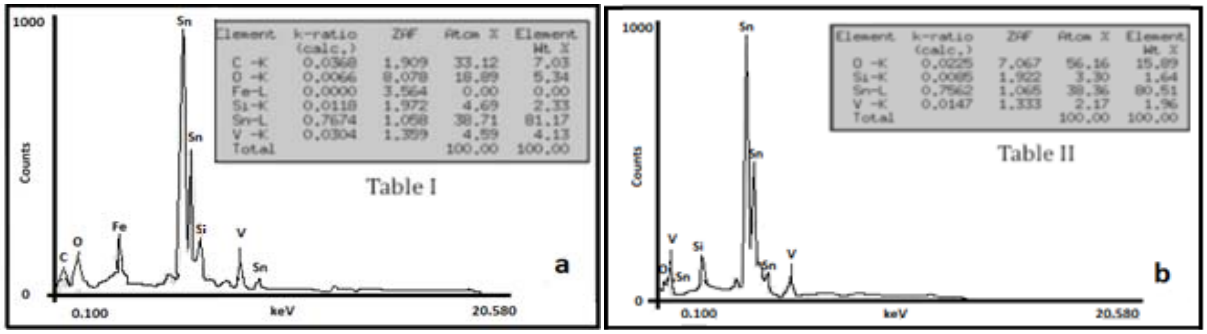
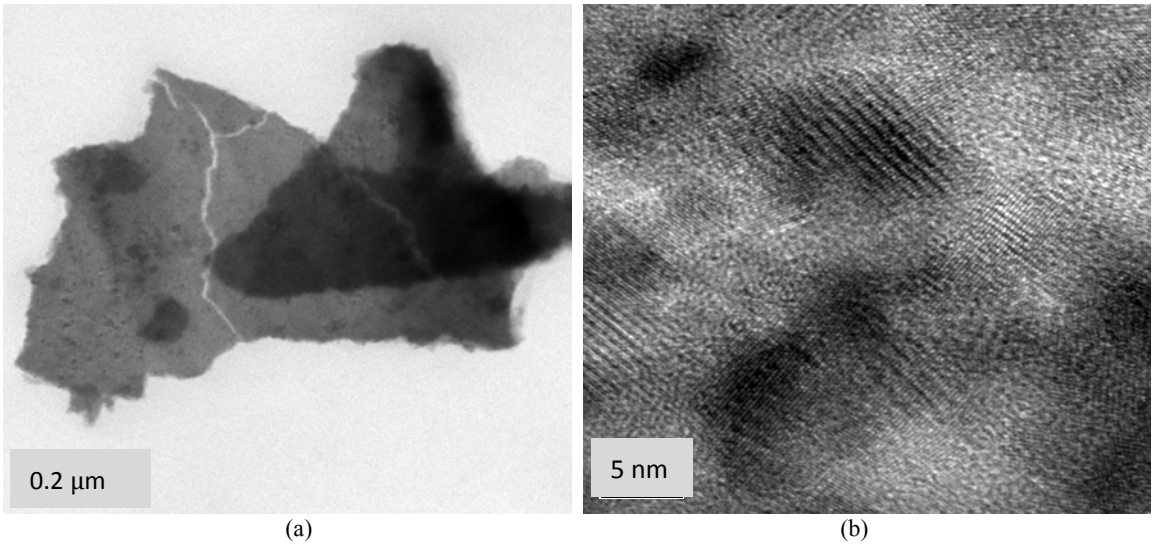



**Fig. 2 A comparison of EDS quantification in tables I and II from samples before and after cyclic voltammetry experiments reveals a lot of vanadium atoms during the electrochemical process, which in turn is related to lots of electrochromic activity in $V_2O_5$ films.**




(a) (b)

**Fig. 3 (a) A bright field TEM micrograph of a pristine micro- $V_20_5$/FTO film. The visible cracks were produced when the sample was stripped out from FTO/glass substrate. (b) A HREM micrograph typical from thin borders appreciated. Amorphous zones between $V_20_5$/FTO grains were detected along the whole sample.**

In Fig. 5a, from a sample deposited without $O_2$, the surface looks regulars dense and compact without inter granular spaces. In Fig. 5b a micrograph from a sample deposited with an $O_2$ atmosphere is presented; the surface looks similar but an increase on $V_2O_5$ grains size can be easily recognized .

SEM micrographs presented in Fig. 4 correspond to films deposited at room temperature before and after cyclic voltammetry experiments. In Fig. 4b, modifications in grains configuration –eroded borders- and new surface details like the cracks and loss of nano grains faceting can be observed along the sample: these changes, are related to mechanical degradation and loss of electrochromic activity as a consequence of mass and charge transport during the electrochemical experiment.

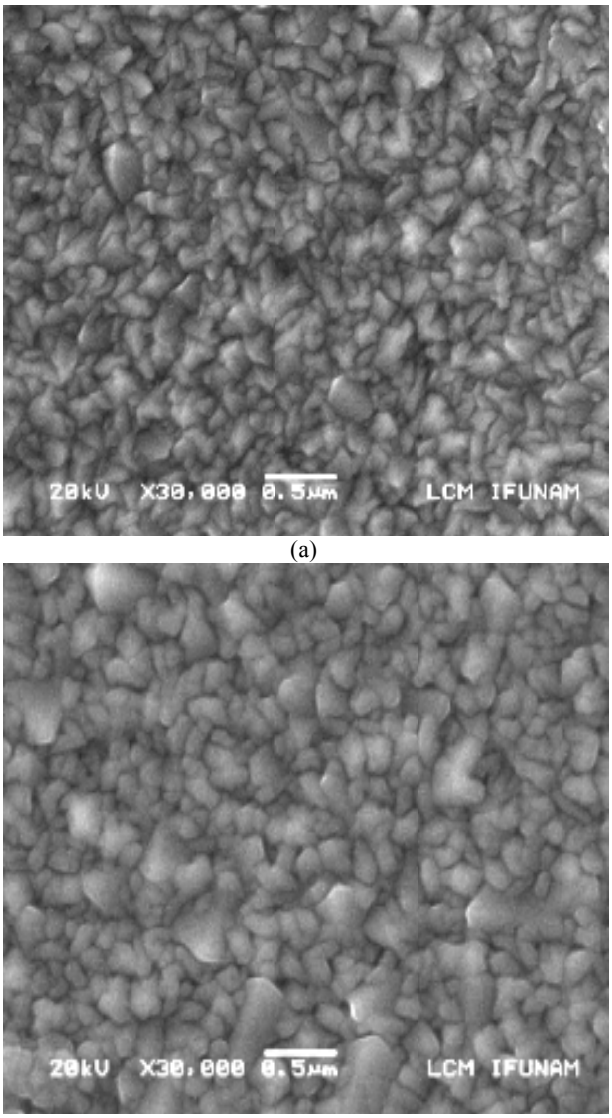



**Fig. 4 SEM micrograph of a pristine $V_2O_5$ films produced (a) without an $O_2$ flux indeposition chamber, (b) with an $O_2$ flux in deposition chamber.**

### *3.4 Optical Properties*

Figs. 6a and 6b compares the optical transmittance for samples deposited without and with $O_2$ on glass and on FTO/Glass substrates respectively.

In Fig. 6a, the $V_2O_5$/Glass sample shows for all the

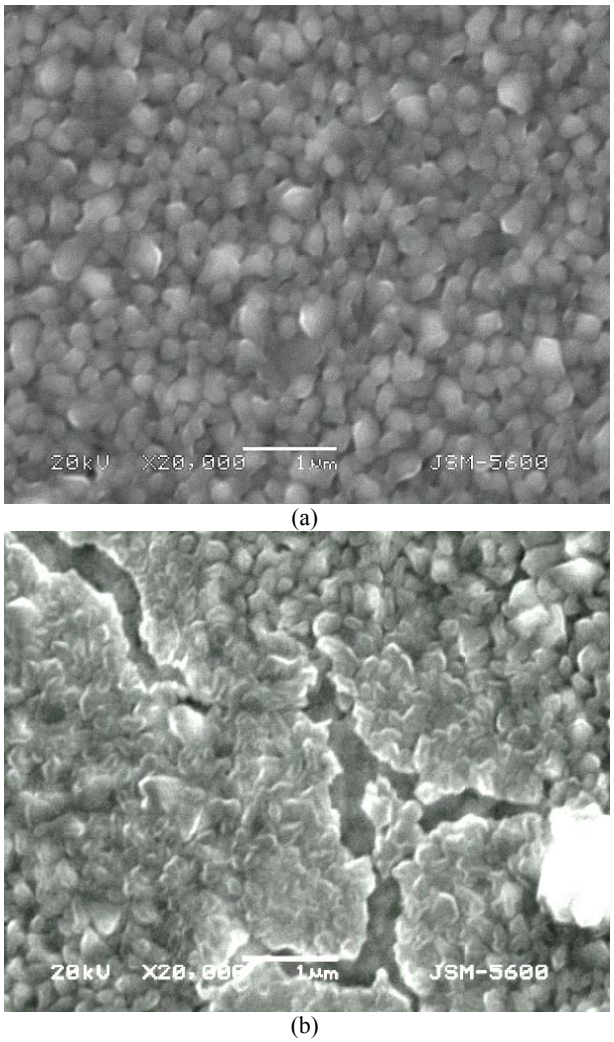
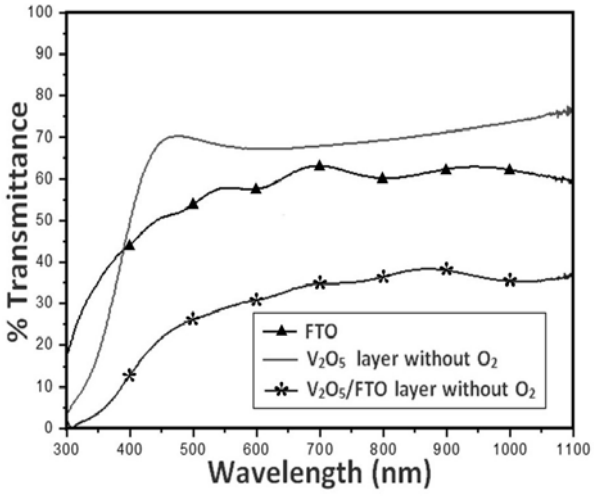
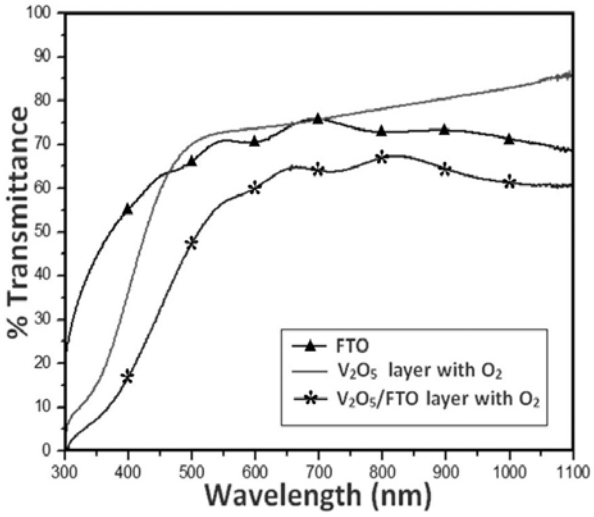



**Fig. 5 (a) A SEM micrograph from a pristine $V_2O_5$/FTO film deposited in a $O_2$ atmosphere . The film looks regular and compact without inter grain spaces. (b) A SEM micrograph from a $V_2O_5$/FTO film after 60 cyclic voltammetry runs. Eroded grain borders and micro-cracks can be observed along the surface.**




(a)




(b)

**Fig. 6 (a) Optical transmittance spectra from $V_2O_5$ samples deposited on glass and on FTO/Glass respectively without $O_2$ (b) Optical transmittance spectra from FTO/Glass and $V_2O_5$ samples prepared on glass and on FTO/Glass respectively with $O_2$.**

wavelengths considered, a higher transmittance than the ones observed for $V_2O_5$/FTO samples. In Fig. 6b, the $V_2O_5$ samples deposited on glass show a higher transmittance than those deposited on FTO/Glass, but with reference to graphics presented in Fig. 6a, the last samples present higher transmittance values for all the wavelengths considered. The deposited $V_2O_5$/FTO films display a reduced transmittance because of their thickness, but coating transmittance shows the same wavelength dependence .

### *3.5 Electrical Properties*

The electrical properties of $V_2O_5$ /FTO films under systematic heating were studied in order to detect variations on physical properties, during process. The electrical resistivity of pristine films deposited at RT and of those heated from 100 to 500 ºC in 100 ºC step were obtained with the Four Point method . In Fig. 7 the behavior of samples deposited without and with $O_2$ is displayed. Noticeable changes in samples electrical resistivity with temperature, were observed: The resistivity grows linearly up to 200 ºC , then a sharp decrease up to close to 255 ºC is observed; after a soft increase up to 300 ºC; , the resistivity, again grows abruptly up to a 500 ºC. The change of resistivity around the 255 ºC is related with the change of a semiconductor to metallic phase [18].

### *3.6 Electrochromic Behavior*

The electrochromic properties of our $V_2O_5$ films were studied in an electrochemical cell with a three electrodes configuration using the CV (Cyclic voltammetry) method. The CV experiments were performed in a potential range running from $E_0$ = – 2,800 mV to $E_1$ = 2,800 mV, using platinum wire as reference electrode with a scanning rate of 1,000 mV/s. Cycling runs, were performed from 1 to 60 cycles respectively and the coloration and bleaching processes at different scanning rates, were observed for all the cases. In Fig. 8 the CV curves for 1, 10, 30 and 60 cycles are presented; it can be observed that cathodic and anodic peaks decrease progressively as the cycle numbers is increased. From SEM micrographs of films deposited at room temperature and after cyclic voltammetry experiments, like the one presented in Fig. 6b, it were detected modifications in grains configuration and surface details that are related with sample degradation and loss of electrochromic activity as a consequence of mass and charge transport and transference during the experiment.

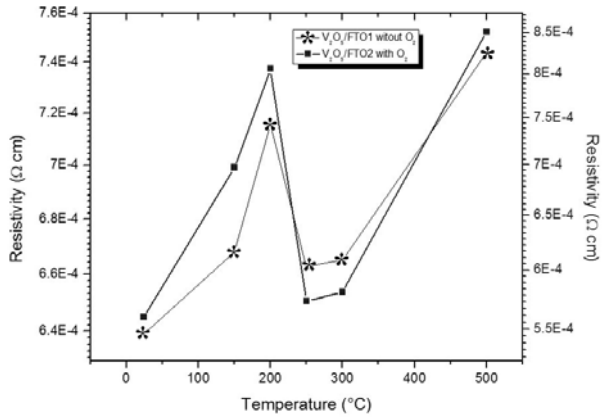



**Fig. 7 Resistivity versus temperature graphics for samples deposited with $O_2$ and without $O_2$. Similar behavior is observed for both samples showing an abrupt change in resistivity values around 255 ºC which is associated to a semiconductor-metal transition.**

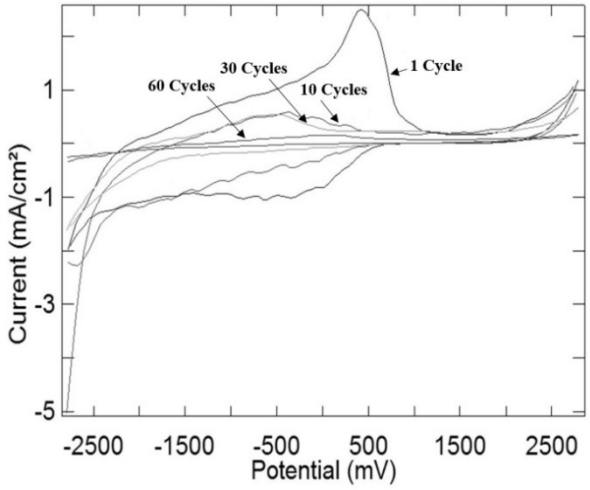



**Fig. 8 Cyclic Voltammetry graphics from a $V_2O_5$/FTO sample deposited in an $O_2$ atmosphere.**

## 4. Conclusions

$V_2O_5$ in thin films configurations were produced by MS in vacuum and in an $O_2$ atmosphere on glass and on FTO substrates. From XRD patterns results the beta-$V_2O_5$ phase was identified. From SEM micrographs it is observed that grains with higher size appears in samples grown in an $O_2$ atmosphere and it is expected to be related with changes observed in optical transmittance and electrical conductivity parameters. An abrupt change in electrical resistivity was observed when $V_2O_5$ samples were heated around 255 ºC and this variation is related with a metal-semiconductor transition. The samples present electrochromic properties, but these disappears after a low number of voltammetric cycles; this behavior is related to structural instability as a consequence of intense mass and charge transport phenomena

## Acknowledgements

The financial support of DGAPA-UNAM Project IN 105514 is appreciated and recognized. Also we thank the financial support of DGAPA–UNAM to the Posdoctoral Position of Dr. Francisco Hernández in our laboratory and recognize the technical assistance of Diego Quiterio and Roberto Hernández in electron microscopy works.

## References

[1] Granqvist, C. G., Green, S. V., Li, S. Y., Mlyuka, N. R., Niklasson, G. A. and Avendaño, E. 2010. "Chromogenics for Sustainable Energy: Some Advances in Thermochromics and Electrochromics." *Advances in Science and Technology* 75: 55-64.

[2] Ottaviano, L., Pennisi, A., Simone, F. and Salvi, A. M. 2004. "RF Sputtered Electrochromic $V_2O_5$ Films." *Opt. Mater.* 27: 307-13.

[3] Krishna, M. G., Debauge, Y. and Bhattacharya, A. K. 1998. "Ammonia Sensing Characteristics of Thin Film Based on Polyelectrolyte Templated Polyaniline." *Thin Solid Films* 312 (1- 2): 116-22.

[4] Wu, G., Du, K., Xia, C., Kun, X., Shen, J. and Zhou, B. et al. 2005. "Optical Absorption Edge Evolution of Vanadium Pentaoxide Films." *Thin Solid Films* 485: 284-9.

[5] RajendraKumar, R. T., Karunagaran, B., SenthilKumar, V., Jeyachandran, Y. L., Mangalaraj, D. and Narayandass, Sa. 2003. "KUV Patterning of Vanadium Pentoxide Films for Device Applications." *Mater. Sci. Semicond. Proc.* 6: 543-6.

[6] Shtmizu, Y., Nagase, K., Miura, N. and Yamazoe, N. 1992. "Electrochromic Properties of Spin-Coated $V_2O_5$ Thin Films." *Solid State Ion* 53-56:490-5.

[7] Julien, C., Haro-Poniatowski, E., Camacho-Lopez, M. A., Escobar-Alarcon, L. and Jimenez-Jarquin, J. 1999. "Growth of $V_2O_5$ Thin Films by Pulsed Laser Deposition and their Applications in Lithium Microbatteries." *Mater. Sci. Eng. B* 65: 170.

[8] Thi, B. N. B., Minh, T. P. and Simona, B. 1996. "Optical and Electrochemical Properties of Vanadium Pentoxide Gel Thin Films." *J. Appl. Phys.* 80: 7041.

[9] Rmana, C. V., Hussain, O. M. and Srinivasulu, N. B. 1997. "Growth and Structure of Electron Beam Evaporated $V_2O_5$ Thin Films." *Mater. Chem. Phys.* 50: 195-9.

[10] Cheng, K.-C., Chen, F.-R. and Kai, J.-J. 2006. "$V_2O_5$ Nanowires as a Functional Material for Electrochromic Device." *Sol. Energy Mater. Sol. Cells* 90: 1156-65.

[11] Bouzidi, A., Benramdane, N., Nakrela, A., Mathieu, C., Khelifa, B. and Desfeux, R. et al. 2002. "First Synthesis of Vanadium Oxide Thin Films by Spray Pyrolysis Technique." *Mater. Sci. Eng. B* 95:141-7.

[12] Boudaoud, L., Benramdane, N., Desfeux, R., Khelifa, B. and Mathieu, C. 2006. "Structural and Optical Properties of $MoO_3$ and $V_2O_5$ Thin Films Prepared by Spray Pyrolysis." *Catal. Today* 113:230-4.

[13] Saitzek, S., Guirleo, G., Guinneton, F., Sauques, L., Villain, S. and Aguir, K. et al. 2004. "New Thermochromic $VO_2$-$CeO_2$ Bilayers for Optical or Electronic Switching Systems." *Thin Solid Films* 449 (1-2): 166-72.

[14] Guinneton, F., Valmalette, J. C. and Gavarri, J. R. 2000. "Nanocrystalline Vanadium Dioxide: Synthesis and Midinfrared Properties." *Optical Materials* 15 (2): 111-4.

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

[16] Cogan, S. F., Nguyen, N. M., Perrotti, S. J. and Rauh, R. D. 1989. "Optical Properties of Electrochromic Vanadium Pentoxide." *J. Appl. Phys.* 66: 1333.

[17] Cui, H.-N., Teixeira, V., Meng, L.-J., Wang, R. and Gao, J.-Y. 2008. "Thermochromic Properties of Vanadium Oxide Films Prepared by DC Reactive Magnetron Sputtering." *Thin Solid Films* 516: 1484-8.

[18] Kang, M., Kim, I., Kim, S. W., Ryu, J.-W. and Park, H. Y. 2011. "Metal- Insulator Transition without Structural Phase Transition in $V_2O_5$ Film." *Applied Physics Letters* 98: 131907.