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V_2O_5 Thin Layers Elaborated By Spray Pyrolysis Deposition Time Effect on the Structural, Optical and Electrochemical Properties

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Abstract: *In this work, we are focusing on the elaboration of the thin layers of vanadium pentoxide (V_2O_5) using the Reactive Chemical Spraying technology in Liquid Phase (RCSLP) on glass substrates. The concentration of the solution was set at 0.05 mol/l, the substrate temperature 450 °C, and the flow rate at 1.5 ml/min. Then, the effect of deposition time (6min - 8min -10min) on the structural, optical and electrochemical properties of thin films of V_2O_5 has been carefully studied. Analysis by X-ray diffraction showed that all layers are polycrystalline, and the preferred orientation of thin V_2O_5 is plane (001) at an angle $2\theta = 20.07°$. SEM images show that the layers are porous. The results were showing also that the transmission of the studied spectral is decreasing when we increase the deposition time. This is due to the higher thickness of the layer which has led to a higher rays absorption. The electrochemical behavior was investigated in (0.5 M $LiClO_4$ propylene carbonate (PC)) solution using a three-electrode cell.*

Keywords: *Pentoxyde vanadium, Thin layers, Reactive chemical spraying, X-ray diffraction, electrochemical.*

1. INTRODUCTION

The thin layer of vanadium pentoxide V_2O_5 has been the subject of research in recent years due to their wide variety of applications involving optical switching [1] and electrochemical devices. Indeed, high electrochemical activity, high stability and ease of vanadium oxide thin films formation by numerous deposition techniques led to its use as lithium batteries with high capacity [2] and as transparent anodes in solar cells [3].

V_2O_5 thin films are prepared by different techniques such as spray pyrolysed [4], radio-frequency sputtering [5], dc-magnetron sputtering [6], flash evaporation [7, 8], sol–gel technique [9], plasma-enhanced chemical vapor deposition [10, 11] and pulsed laser deposition [12]. In this paper, we analyzed the effect of temperature and the deposition time of the films on structural properties, Morphology, optical properties and electrochemical investigations.

2. METHODS

2.1. Growth of V_2O_5

The thin films of V_2O_5 are deposited onto glass substrates heated at 450°C from an aqueous solution containing vanadium chloride (VCl_3) using the spray pyrolysis method. The experimental set-up for this has been described previously [7]. The concentration of the solution was set at 0.05mol/l, the flow rate at 1.5 ml / min and different deposition time (6 min-8min-10min). For the electrochemical investigation, the films were deposited on ITO-coated glass substrates.

2.2 Characterization

The structural characterizations are performed using X-ray diffraction (XRD) with Cu Kα radiation (λ=1.5406 A), the patterns were recorded over the angular range 12–80° (2θ). Morphology of as-deposited thin film was observed using FEI Quanta 200 Brand scanning electron microscope. Optical measurement were carried out using the Spectrophotometer jasco uv/vis/nir V570 in the wavelength range (350 - 2200nm). The electrochemical experiments were performed using a VoltaLab systems withVM4. A platinum sheet was used as a counter electrode. The voltage was measured with respect to the saturated calomel reference electrode (SCE).

3. RESULTS AND DISCUSSION

3.1. Structural Properties

Figure 1 shows the XRD patterns for samples grown at different time deposition (6 min; 8 min; 10 min)

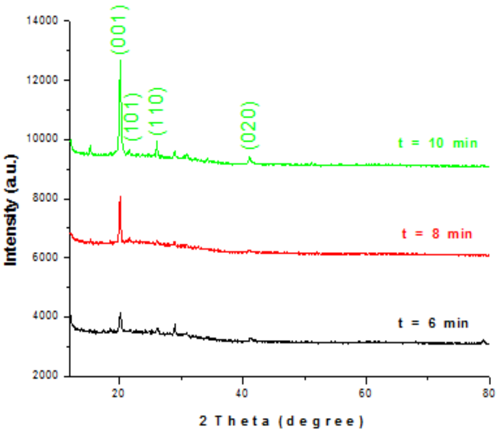

Fig1. *X-ray diffraction spectra of V_2O_5 samples at different deposition time (t)*

Analysis by X-ray diffraction showed that all layers are polycrystalline and have orthorhombic structure. The preferred orientation of thin V_2O_5 (001) at the angle $2\theta=20.07°$, indicates the preferred orientation along the crystallographic C axis perpendicular to the substrate and which is the main line of the orthorhombic structure. It can be concluded that the crystallinity of V_2O_5 thin films is improved gradually upon the deposition time increase.

For evaluation of lattice parameters we have used the relation:

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}}} \qquad (1)$$

With a#b#c for orthorhombic lattice. In this relation (h, k, l) are miller indices of reflector plans appearing on the diffraction spectra and d_{hkl} their inter-reticular distances. The obtained values of lattice parameters for the four films and the unit cell volumes calculated for each sample are summarized in the Table 1

Table1. *Lattice parameters, unit cell volume and microstrain εzz of the deposited V_2O_5 films. The data of V_2O_5 (JCPDS) are taken from the JCPDS card.*

sample	Lattice parameters			Cell volume (A°^{3})	εzz
	a (A°)	b (A°)	c (A°)		
t=6min	11,490	3,550	4,41	178,97	1,40
t=8min	11,522	3,564	4,413	179,02	1,56
t=10min	11,382	3,575	4,422	179,98	1,77
V2O5 (JCPDS)	11,498	3,545	4,345	177,10	---

The lattice parameters of the layers show differences in regards to those of V_2O_5 (JCPDS) [12] . In particular the length of the C axis. The C parameter value is greater than that of V_2O_5 (JCPDS), this is resulting in a volume expansion of cells [12].

Table 1 reports the values of the film strain along the c-axis, εzz, calculated by the following equation:

$$\varepsilon_{zz} = \frac{C - C_0}{C_0} \qquad (2)$$

Where C and C_0 are the lattice parameters of the strained and unstrained V_2O_5, respectively. The films deposited at (t= 6 min; t=8min; t=10min), the observed residual strain decreases by increasing the film thickness, in agreement with the literature [12].

3.2. Morphology

SEM images show the evolution of morphology with deposition temperature and the deposition time. The deposited V_2O_5 film has a very porous nature, and particle shape is three-dimensional [13].

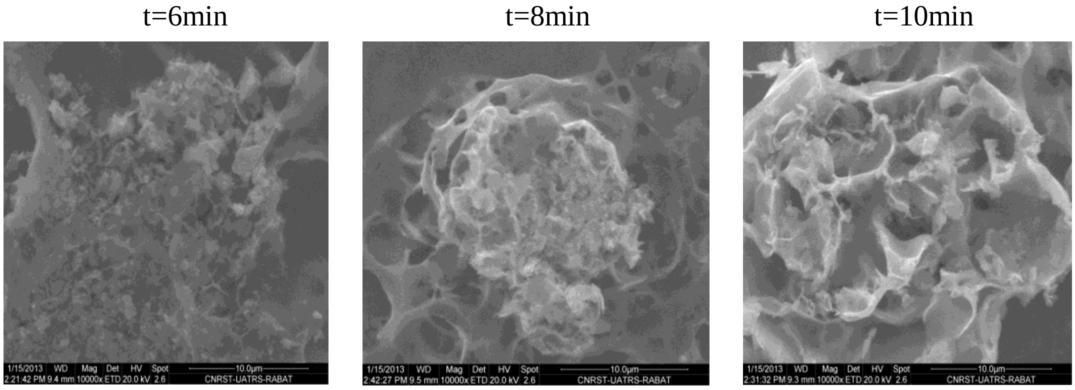
t=6min t=8min t=10min

Fig2. *SEM of V_2O_5 samples at different deposition time (t)*

3.3. Optical Properties

The spectral transmission of V_2O_5 films prepared with these conditions Ts=450°C, C=0,05M and t=6 min, t = 8 min, t = 10min are shown in the figure 3, the Optical transmission for as grown films was measured in the range 300 - 2000nm using a spectrophotometer. For the deposition time equals to 6 min, the spectra shows a plate reaches 32% in the visible region and a slight decreases in the near-infrared range (NIR).For the deposition time equals to 8 min, the spectra shows a plate reaches 19% in the visible region and a slight decreases in the NIR. For the deposition time equals to 10 min, the spectra shows a plate reaches 14% in the visible region and a slight decreases in the NIR, the transmission was low but this is normal as the solution concentration was high. The same results were reported by Bouzidi et al. [14]. The results were showing also that the transmission of the studied samples is decreasing with the deposition time increase. This is due to the higher thickness of the layer which has led to a higher rays absorption.

The concentration increase of free electrons in the thin films conducts to a decrease of NIR region. The transmittance in the infrared zones is also inversely related to the concentration due to the interaction between free electrons and the incident long wavelength [15].

The optical absorption coefficient (α) is calculated from the relation:

$$\boldsymbol{\alpha = \frac{1}{t\left[ln(\frac{100}{T})\right]}} \qquad (3)$$

Where, T is the measured transmittance and t is the film thickness. By linear fitting and extrapolating the line to the abscissa (Plot of $(\alpha h\nu)^2$ vs $(h\nu)$), we can get the direct band gap (Eg). (Fig.4). The deposition time influences on the direct gap energy. We noticed that the direct optical gap decreases when increasing the deposition time, at T=6min Eg=2,48ev, at T=8min Eg = 2,46ev, at T=10min Eg= 2,44ev.

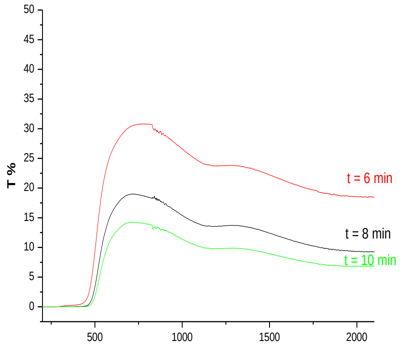

Fig3. *Transmission spectra of V_2O_5 thin films at different deposition time (t)*

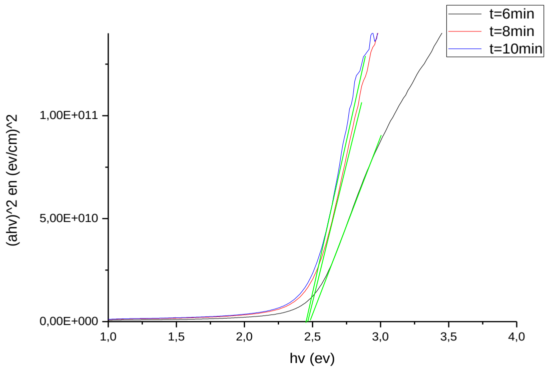

Fig4. *Direct band gap estimation of V2O5 samples at different deposition time (t)*

3.4. Electrochemical Investigations

The electrochemical characteristics of V_2O_5 thin films deposited on ITO are studied by recording the cyclic voltammetry (CV) in a propylene carbonate (PC) solution with 0.5 M of the lithium perchlorate trihydrate ($LiClO_4$).

Figure 5 shows the first voltammetry cycle plot between -1.5V and +1.5V of V_2O_5/ITO thin film elaborated at substrate temperature of 450 °C. It reveals that the sprayed film is capable of Li^+ intercalation/deintercalation process in accord with many works onV_2O_5 thin films [16,17]. The reduction–oxidation reaction can be expressed as:

$$V_2O_5 + x\,Li^+ + x\,e^- \Leftrightarrow Li_xV_2O_5 \qquad (4)$$

In order to improve the electrochemical properties we have increased deposition time. Figure 5 presents the difference between the first voltammetry cycle of films elaborated at t=6min, t=8min and t=10min. It shows that the increase of deposition time increases the area of the cycle which indicates a greater capacity of insertion/extraction of lithium ions.

The thin film elaborated at t=10min shows an open cyclic compared to the other film, and the curve shape illustrates the existence of two large anodic current peaks A1 and A2 corresponding to the oxidation states of thin film and the cathodic current peak C1 corresponding to the reduction state of the thin film. We can conclude that, the deposition time, illustrates significant reduction/oxidation phenomena for the optimal conditions, indicating a good voltammetric response. We can see that increasing deposition time favours the capability of Li^+ intercalation/desintercalation process.

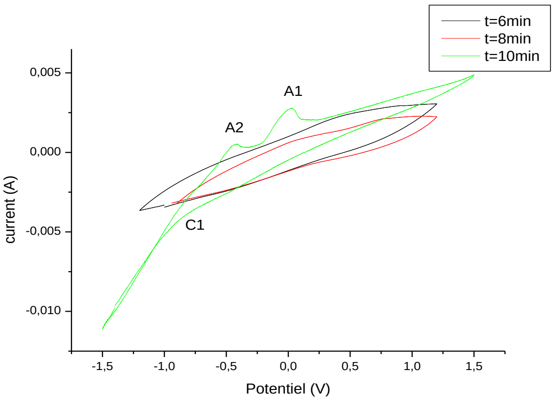

Fig5. *Cyclic voltammograme of V_2O_5 on ITO glass, electrode which applied voltage between -1.5 and +1.5V*

4. CONCLUSION

In this work we have studied the elaboration of V_2O_5 films using spray pyrolysis technique at substrate temperatures of 450 °C, and a deposition time of 6-8-10min with concentration equals to 0,05 mol/l. Analysis by X-ray diffraction showed that all layers are polycrystalline, and the preferred orientation of thin V_2O_5 was plane (001) at an angle 2θ = 20.07°. SEM images show that the layers are porous. The results were showing also that the transmission of the studied spectral is decreasing with the deposition time increase. This is due to the higher thickness of the layer which has led to a higher rays absorption. Electrochemical properties show that the increase of deposition time increases the area of the cycle which indicates a greater capacity of insertion/extraction of lithium ions.

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