Relationship Between Structural and Optical Properties in Vanadium Pentoxide

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Abstract. Spray pyrolysis technique (SPT) and radio-frequency magnetron sputtering (RF-MS) were used to obtain vanadium oxide \((V_xO_y)\) layers. The surface morphology was visualized using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Further, the microstructure was assessed by means of X-ray diffraction (XRD), showing the formation of orthorhombic \(V_2O_5\) (\(\alpha-V_2O_5\)) with high crystallinity by SPT. On the other side, RF-MS at low substrate temperature led to \(\alpha-V_2O_5\) with low crystallinity, even at 800 swipes which according to the Kiessig interference fringes from X-ray reflectivity indicates a film thickness of 70 nm. Finally, diffuse reflectance spectroscopy (DRS) absorbance was used to investigate the optical properties for the obtained samples, noting important differences regarding the bandgap energy between SPT and RF-MS depositions. To explain the observed discrepancies, X-ray photoelectron spectroscopy (XPS) was performed, thus obtaining a correlation of the bandgap to the oxidation state of vanadium ions.

Key-words: RF magnetron sputtering; spray pyrolysis technique; vanadium oxide; X-ray diffraction.
1. Introduction and Preliminary Results

Vanadium oxides compounds have received a constantly growing interest in materials science, due to their ability to tune the material properties according to the oxidation state \((V^{2+}, V^{3+}, V^{4+}, \text{and } V^{5+})\) [1, 2] and the conducted studies revealed a plethora of applications derived from vanadium oxide materials. For instance, thin films of \(VO_2\) and \(V_2O_5\) have been found to show good thermochromism in the infrared region and moreover, the metal-insulator transition (MIT) with the change in temperature is related to thermo and electrochromic applications, such as smart windows [3], ultra-fast nanoelectronic switches [4] transistors [5], thermoelectric devices [6]. Vanadium pentoxide \((V_2O_5)\) is the most stable compound and has attracted much attention owing to its unique electronic, chemical, and optical properties, arousing interest in the broadband photodetectors [7], gas sensors [8, 9] and electrochromic devices [10–12].

The structural properties of \(V_2O_5\) play a critical role in determining its optical properties, such as its absorption, reflectance, and transmission spectra. One important structural property of \(V_2O_5\) is its crystal structure, which can be varied depending on the synthesis method and processing conditions. For example, \(V_2O_5\) can exist in several different crystal structures, including orthorhombic, monoclinic, and amorphous phases, each with different optical properties [13]. Among these, the orthorhombic phase of \(V_2O_5\) \((\alpha-V_2O_5)\) has been shown to have a high degree of crystallinity and exhibits strong absorption in the ultraviolet and visible regions of the electromagnetic spectrum, which makes it suitable for use as a UV-blocking material in coatings and sunscreens. Another important structural property of \(V_2O_5\) is its morphology, which also affects its optical properties. For instance, \(V_2O_5\) nanostructures have been shown to exhibit enhanced optical properties compared to their bulk counterparts, due to their high surface area and increased light scattering and absorption. In addition, one-dimensional structures have been shown to exhibit strong near-infrared absorption, which makes them attractive for use in energy storage and photovoltaic devices [14]. The optical properties of \(V_2O_5\) can also be influenced by doping with other elements, which can alter the electronic structure and bandgap of the material. For example, the optical properties of \(V_2O_5\) can be tuned by introducing W or Mo dopants, which can shift the absorption spectra to longer wavelengths and improve the material’s charge transport properties [15, 16]. Therefore, the structural properties of \(V_2O_5\), such as its crystal structure, morphology, and doping, are closely related to its optical properties and can be tailored for specific applications in optical devices, energy storage, and catalysis. Furthermore, it was suggested that the regular stacking of the atomic planes along \((001)\) in crystalline \(V_2O_5\) is very favorable for the intercalation of hosts for Li ions, like in rechargeable batteries [17, 18] since such a well-aligned structure would enhance the \(Li^+\) diffusion through the solvent. Moreover, amorphous \(V_xO_y\) became popular for Li- and Na-ion batteries [19], high-energy Li-ion anodes [20], or positive electrode in rechargeable aluminum battery [21].

Whereas crystalline vanadium oxide thin films can be obtained by RF-magnetron sputtering or pulsed laser deposition at elevated substrate temperatures [22], amorphous vanadium oxide thin films can be obtained by electrochemical oxidation [23], reactive sputtering [24], using a combination of sol-gel processing paired with electrochemical deposition [25], atomic layer chemical vapor deposition [19], atomic layer deposition [26], or gas impulse magnetron sputter-
ing [21]. In order to have $V\text{O}_x$ layers with high specific surface area, different methods were proposed to obtain vanadium oxide in nanostructured form, such as electrospinning of $V_2\text{O}_5$ nanofibers, electrostatic spray-deposition, deposition of $V_2\text{O}_5$ nanowires from chemical vapor transport or spray pyrolysis technique [27].

One of the most important parameters for assessing the properties of materials is the bandgap energy ($E_g$), which is affected by the crystallographic structure, stoichiometry, internal strain, crystal quality or dimensionality (i.e. thin film/nanostructured) or oxidation state [1]. The electronic structure of $V_2\text{O}_5$ has been the subject of intensive studies and various theoretical calculations of band structure that include both semiempirical and ab initio techniques [28–30] and it was found a large variation in the visible region [1, 31].

This paper represents an extension of our recent published paper [32], in which we presented the preparation methods and some preliminary characterization of vanadium oxide layers, without to explain different observed bandgaps values. Herein, the morpho-structural properties of $V_2\text{O}_5$ samples obtained by spray pyrolysis technique (SPT) and radio-frequency magnetron sputtering (RF-MS) in correlation with their optical properties are presented. The crystal structure was resolved by X-ray diffraction (XRD) by Rietveld refinement, while the band gap energy was evaluated by diffuse reflectance spectroscopy (DRS) and Kubelka-Munk (K-M) transformation. An explanation of the relative high value of the band gap energy for the samples obtained by RF-MS was provided considering the presence of $V^{4+}$ oxidation state, as proved by X-ray photoelectron spectroscopy (XPS) investigations.

The next section presents the experimental details for the SPT and RF-MS, as well as the characterization tools. Then, Section 3 is dedicated to the application of different characterization tools, as follows: scanning electron and atomic force microscopy (SEM/AFM), XRD/XRR, DRS and XPS to investigate the sample microstructure and the optical properties. Section 4 concludes this paper.

2. Experimental Details

During the SPT deposition, a custom-made spray pyrolysis setup was used, and more details can be found in previously reported work of the same group [33]. Fluoride tin oxide (FTO) coated glass substrates were used for deposition, keeping a temperature of 250 °C, employing different quantities and concentrations for the precursor: (5mL, 0.01M); (10mL, 0.01M); (5mL, 0.02M); (10mL, 0.02M). After deposition, the samples were subjected to a thermal treatment of 400 °C, following the procedures described in [34]. In the RF-MS deposition case, silicon (Si) substrates were used at constant growth parameters (Ar:N = 20:1 in sscm, power RF = 300 W, deposition temperature = 60 °C, chamber pressure = 5 mTorr, power = 300 W), while the number of the swipes was varied from 100 up to 800 swipes.

Grazing incidence XRD investigations were performed using a 9 kW Rigaku SmartLab diffractometer in $2\theta$ mode, keeping the incidence angle at 0.5 °. X-ray reflectivity (XRR) spectra were recorded in $\theta/2\theta$ mode in a medium resolution configuration with open detector. Scanning electron microscope (SEM) characterization was performed using a field emission scanning electron microscope Nova NanoSEM 630 (FEI Company, Hillsborough, OR, USA). The AFM micrographs have been acquired using Ntegra Aura (Nt-MDT) equipment, operated in semicontact (intermittent-contact) mode. Diffuse reflectance spectroscopy (DRS) was performed using an integrating sphere placed inside a FLS920 spectrometer (Edin. Inst. Ltd, UK) equipped with 450 W Xe lamp and the excitation light was dispersed by a monochromator with 1800 grooves/mm
grating (0.1 nm resolution). X-ray photoemission spectroscopy (XPS) spectra were recorded on a Sigma Surface Science photoelectron spectrometer equipped with a 160-mm hemispherical energy analyzer with a 1D detector (ASPECT) and using an Al K$_\alpha$ X-ray source at 13 kV at a power of 200 W. All spectra were fitted using a Shirley type background and a Lorentzian-Gaussian peak shape.

3. Results and Discussion

3.1. Scanning electron and atomic force microscopy characterization

To study the surface morphology of the obtained samples by SPT, top-view SEM micrographs were recorded according to Fig. 1 (a).

The SEM micrographs show the presence of the large grains when a low precursor quantity was used, while for larger precursor quantity the surface morphology consists of a combination of irregular walls with high aspect ratio and granular nanostructured flat film regions. The walls width is below 1 µm, while the length reaches up to 10 µm. In previous studies of surface morphology for vanadium oxide obtained by SPT, it was observed a close dependence of width of the walls on the deposition conditions, as reported in [33]. More specifically, it was found that the width increased with the precursor quantity from 300 to 800 nm, and correlate also with a better crystallization at higher precursor quantity. Overall, the samples obtained through RF-MS exhibit a smooth surface composed of fine and uniform grains, even after 800 cycles (see Fig. 1b). However, as the number of cycles increases and the films are becoming thicker, the surface tends to develop additional globular agglomerations that grow in size and density. The results
presented in the next section suggest that the different crystal quality could be responsible for the different surface morphology features observed by microscopic techniques.

3.2. X-ray diffraction and reflectivity

Accordingly, the microstructure of each sample was investigated by grazing incidence X-ray diffraction as shown in Fig. 2 (a).

Fig. 2. (a) Grazing incidence XRD patterns for the investigated samples and FTO substrate. The identification of the diffraction peaks was made using ICDD database, thus: $\alpha-V_2O_5$ (diamond symbol), $NH_4VO_3$ (star) and FTO substrate (star). (b) Experimental data (black points) and Rietveld fit (red line), as well as the difference between the experimental and calculated data (grey line). In the inset are presented the fitting parameters, $R_{wp}$ and $S$. (c) Experimental XRR data (points) with the simulated data (line) and (d) GI-XRD patterns for RF-MS samples.

One can observe that the X-ray diffraction patterns present a large number of diffraction peaks. Most of them are attributed to FTO substrate (black line) and other diffraction peaks located at 20.35°, 21.59°, 32.10°, 33.75°, 42.00°, 47.71° and 48.84° are unambiguously as-
signed as (001), (101), (011), (002), (600) and (021) reflections of $\alpha - V_2O_5$ phase with $a = 1.148$ nm, $b = 0.436$ nm, and $c = 0.355$ nm, that belongs to 47:Pmmm space group with orthorhombic symmetry (diamond symbol). Moreover, the unreacted metavanadate compounds from the synthesis processes are also detected by XRD at 10 mL. It seems that in the case of 5 mL at 0.01 M concentration the film was not yet formed at low precursor concentration (green line). As recently reported in [35], the strong intensity of (001) reflection at 20.35$^\circ$ suggests a regular stacking of imperfect ab planes built up of vanadyl oxygen and that the c-axis is perpendicular to the surface sample [36]. In our recent work, we have shown that the texture coefficient (i.e. preferential orientation) along (001) reflection is closely related to the inserted charge density in $\alpha - V_2O_5$, key parameter for the electrochromic and charge storage devices [33]. Obviously, the different synthesis parameters influence the formation and the crystal quality of $V_2O_5$ films, as well as the texture coefficient. An assessment of the microstructural features was made using Rietveld refinement method. In this framework, the pattern fitting is performed over a broad angular range, based on reasonable initial approximation of unit cell dimensions or coordinates of all atoms in crystal. The theoretical profile, $y_{i}^{calc}$, has the following expression [37]:

$$ y_{i}^{calc} = A(2\theta) \sum_{n} s_{n} \sum_{h} P_{n,h} I_{n,h} \phi_{n}(2\theta_{i} - 2\theta_{h} - T(2\theta_{i})) + y_{b}(2\theta_{i}) \tag{1} $$

Here, $s_{n}$ is the scale factor, $2\theta_{h}$ the Bragg angle, $A(2\theta)$ the absorption and irradiation correction, $P_{n,h}$ the preferred orientation correction, $I_{n,h}$ the integrated intensity function, $T(2\theta_{i})$ the angular correction, and $y_{b}(2\theta_{i})$ the background function. During the Rietveld refinement, multiple features of the patterns were considered. For instance, the background was modeled with a B-spline function, the peak shift with the shift axial displacement model, the peak shapes using pseudo-Voigt fits, while the preferred orientation with the March-Dollase function. The fitting of the theoretical profile, $y_{i}^{calc}$, was performed over the experimental data using a least-squared minimizing procedure and a set of numerical figures of merit (FOM’s): reliability factor ($R_{p}$), the weighted parameter ($R_{wp}$), the scale factor ($S$), the expected profile residual, $R_{e}$ and the goodness of the fit, $\chi^{2}$.

In Fig. 2 (b), the red line depicts the Rietveld data with the corresponding $R_{wp}$ and $S$ fitting, which indicate the fitting accuracy of the refinement. The values of the mean crystallite size, the unit cell parameters and the average lattice strain are presented in Table 1. The results indicate that the unit cell parameters are not affected by either solution quantity or molarity. However, a smaller mean crystallite size, accompanied by a higher lattice strain, was found at the concentration 5 mL with 0.02 M molarity. Further, when the molarity increased, the mean crystallite size also increased, and at the same time, the lattice strain became smaller.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a, b, c (nm)</th>
<th>$\tau$ (nm)</th>
<th>$\varepsilon$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5ml.0.01M No crystalline film formed</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>5ml.0.02M</td>
<td>1.18, 0.34, 0.43</td>
<td>17.8</td>
<td>0.26</td>
</tr>
<tr>
<td>10ml.0.01M</td>
<td>1.18, 0.34, 0.43</td>
<td>19.6</td>
<td>0.21</td>
</tr>
<tr>
<td>10ml.0.02M</td>
<td>1.18, 0.34, 0.43</td>
<td>18.7</td>
<td>0.15</td>
</tr>
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In the case of RF-MS samples, XRR and XRD curves were used to investigate how the number of swipes affects the layer’s thickness and crystal quality, when the swipe number increased from 100 to 200, then to 400, reaching to 800 according to Fig. 2 (c) and (d).
In each case, the reflectivity profiles present periodic fringes that stem from the interference at the boundary at the layer and substrate and are called Kiessig fringes. Their period, $\Delta \theta$ in radians is related to the layers thickness, $\tau$ through the following relation [38]:

$$\tau = \frac{\lambda}{\Delta \theta}$$  \hspace{1cm} (2)

where $\lambda$ is the X-ray wavelength (0.154 nm).

According to the period of interference fringes, the thickness increases from 7 to 70 nm when the number of the swipes is modified from 100 to 800. The thickness of each sample is illustrated in Table 2.

**Table 2.** Number of swipes, thickness calculated from XRR and the mean crystallite size determined from the Rietveld refinement

<table>
<thead>
<tr>
<th>Swipes</th>
<th>Thickness (nm)</th>
<th>Mean crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>6.8</td>
<td>–</td>
</tr>
<tr>
<td>200</td>
<td>15.9</td>
<td>5.8</td>
</tr>
<tr>
<td>400</td>
<td>32.5</td>
<td>6.4</td>
</tr>
<tr>
<td>800</td>
<td>70.1</td>
<td>7.1</td>
</tr>
</tbody>
</table>

Concomitantly, GI-XRD data indicate the formation of the (001) $\alpha-V_2O_5$ and the diffraction peak becomes narrower at higher thickness, since the crystalline domains become also higher, as it will be shown by Scherrer’s equation. This further implies the emergence of (101) and (002) reflections at higher thickness. The Scherrer’s equation gives the relationship between the size of the crystalline domains, $\tau$ in respect to the peak broadening, and $\beta$ expressed in radians in the following way:

$$\tau = \frac{k \lambda}{\beta \cos \theta}$$  \hspace{1cm} (3)

where $k$ is the shape factor, taken equal to 0.93 in this study, $\lambda$ is the X-ray wavelength and $\theta$ is the angular position of the (100) diffraction peak. According to Scherrer’s equation, there is a variation of the mean crystallite size from amorphous domains to crystalline domains with size of 7 nm (e.g. 800 swipes). The values of the crystalline domains size are tabulated in Table 2. That indicates that, at the low temperature of the substrate ($\sim 60^\circ$C), the deposited material may be just sticking to the Si/SiO$_2$ substrate surface, with almost no surface diffusion [22]. The substrate temperature is not high enough to provide sufficient thermal energy to the ad-atoms to find the locations for further bonding, resulting in structure with poor crystal quality. On the other hand, sharp diffraction peaks were found in SPT deposition, for which the samples were obtained at a substrate temperature of 250 $^\circ$C, further subjected to a thermal treatment at 400 $^\circ$C in O$_2$ atmosphere. Previous XRD studies showed that the deposition of crystalline V$_2$O$_5$ phase occurs at around 200 $^\circ$C in the case of d.c. reactive magnetron sputtering [39].

### 3.3. Optical measurements

In order to establish the influence of the microstructure in the optical properties, the diffuse reflectance spectroscopy (DRS) and Kubelka-Munk (K-M) transformation were employed, to estimate the optical band gap in SPT deposition shown in Fig. 3 (a).
For this purpose, it is necessary to evaluate correctly the interband transition in the investigated samples, namely direct, indirect or both. The available literature on the bandgap of V$_2$O$_5$ is vast and shows that the bandgap is affected by thin film deposition technique, thickness, substrate type or non-stoichiometry [1]. In most cases, it was found that a direct allowed transition is the most probable one in α−V$_2$O$_5$. However, transmission measurements conducted by [40] for sputtered α−V$_2$O$_5$ indicated two distinct interband transitions, implying direct and indirect transition. In particular, since α−V$_2$O$_5$ obtained by SPT is crystalline, a direct interband transition was considered in Kubelka-Munk transformation. On the other hand, considering the low crystallinity of VO$_x$ in the case of RF-MS samples and the presence of V$^{4+}$ ions in these samples (as it will be proved by XPS), the interband transition was considered rather indirect. According to the calculations, the band gap falls within the range 2.20 eV – 2.40 eV, which is a typical range for vanadium pentoxide deposited using SPT [41], suggesting the presence of pure α−V$_2$O$_5$. Studies have reported the bandgap of V$_2$O$_5$ films synthesized by spray pyrolysis to be in the range of 2.2-2.6 eV [42–44]. Mousavi et al. [45] observed that for V$_2$O$_5$ films prepared by spray pyrolysis $E_g$ changes with the substrate temperature ($T_{sub}$), considering also a direct interband transition. When $T_{sub}$ increases, the $E_g$ decreases gradually from 2.46 to 2.22 eV, due to the modification of the extinction coefficient at different temperatures. The authors reported that the optical bandgap of the V$_2$O$_5$ films ranged from 2.4 to 2.6 eV, depending on the deposition parameters. In the present study case, the substrate temperature was kept constant, and the modifications could be explained by taking into account different synthesis parameters. More specifically, one can observe that the band gap of the material reported here is quite low and decreases from 2.38 eV to 2.36 eV and then to 2.20 eV when the precursor quantity is high. This can be associated to the higher thickness and improved crystallinity. On the other hand, the RF-MS samples present two regions. At high wavelength, it can be observed an absorption peak given by Si ($E_g = 1.1$ eV), while V$_2$O$_5$ layer absorbs at lower wavelength. It should be mentioned that the samples obtained at 100 and 200 swipes could not be analyzed, due to their small thickness, *i.e.* 6.8 nm and 15.9 nm, respectively. In this case, we chose the thicker V$_2$O$_5$ samples. Fig. 3 (a) gives the evolution of the absorption spectra with V$_2$O$_5$ thickness. Whereas the band

![Fig. 3. Diffuse reflectance spectra for the investigated samples obtained by (a) SPT and (b) RF-MS.](image-url)
gap of the SPT samples was found in the range of 2.2 and 2.4 eV, in the case of RF-MS the band gap is significantly wider, with values ranging from 2.82 eV to 2.90 eV at 70.1 nm. Studies that have reported optical bandgap values for RF sputtered $V_2O_5$ films on Si reported bandgaps ranging from 2.5 to 3.3 eV [46–48]. The origin of the UV absorption was extensively studied by Meyn et al. [49], who reported that the UV light absorption in the oxides can be enhanced by tetravalent vanadium ion $V^{4+}$ presence. Thus, it is considered that the PL properties of vanadium oxide thin films strongly depend on the oxidation state. Furthermore, relative high values for band gap in RF-MS can be explained considering the low substrate temperature during the sample deposition. Kang et al. [40] showed that the interband transition is dependent on the substrate temperature during deposition, and the bandgap decreases as the substrate temperature increases in RF-MS deposition. To explain the higher band gap energy at high thickness for the RF-MS sputtered films, it was studied the dependence of the oxidation state with the thickness by XPS.

### 3.4. XPS

XPS investigation was carried out on $V_2O_5$ 2/Si samples, to obtain information related to the oxidation state of vanadium ions. Fig. 4 shows the XPS spectra recorded at 100, 200, 400 and 800 swipes.

![Fig. 4. Experimental XPS spectra for the obtained samples by RF-MS at 100, 200, 400, 800 swipes (black points) and the corresponding fits.](image)

It is revealed the presence of V 2$p$ doublet and the fitting were performed using a mixed Lorentzian-Gaussian function. Due to spin splitting, the V 2$p_{3/2}$ and V 2$p_{1/2}$ signal areas have a fixed 2:1 ratio and fixed shift of 7.4 eV. The $V_2O_5$ presence is proved by given by the spin-orbit splitting of approximately 7.5 eV between V 2$p_{3/2}$ and V 2$p_{1/2}$ orbitals [25], [50]. The V 2$p_{3/2}$ and V 2$p_{1/2}$ were deconvoluted using $V^{4+}$ (binding energy, $BE = 515.5$ and 523 eV) and $V^{5+}$ ($BE = 517.1$ and 524.7 eV) oxidation states. The binding energy values for vanadium oxides...
are in a good agreement with the previous work on vanadium pentoxide [51, 52]. The integral areas provided by the deconvolution procedure normalized at the atomic sensitivity factors were used to determine the distribution between the V$^{4+}$ and V$^{5+}$ states in the V 2p signal [53]. Thus, it was shown that the oxidation state depends by the layer thickness. Whereas in the thinnest sample has the smallest V$^{4+}$ content, V$^{4+}$($\%$) = 8.9%, in the case of the thickest one, V$^{4+}$($\%$) becomes 18.5%. A higher V$^{4+}$ content in the thick sample could be responsible for the observed band gap in this sample (e.g. 2.9 eV), while the other samples have the band gap around of 2.83 eV. Overall, it is suggested the close relationship between the oxidation state and the observed band gap in V$_2$O$_5$.

4. Conclusions

Spray pyrolysis technique, SPT, and radio-frequency magnetron sputtering, RF-MS, were used to obtain vanadium oxide, V$_x$O$_y$, thin films. The surface morphology was visualized using scanning electron microscopy, SEM, and atomic force microscopy, AFM. Further, the microstructure was assessed by means of X-ray diffraction, XRD, showing the formation of orthorhombic V$_2$O$_3$ ($\alpha$ − V$_2$O$_3$) with high crystallinity for films made by SPT. On the other side, RF-MS at low substrate temperature led to $\alpha$ − V$_2$O$_3$ with low crystallinity, even at 800 swipes (i.e. 70 nm thickness estimated according to the Kiessig interference fringes from X-ray reflectivity). Finally, diffuse reflectance spectroscopy, DRS, absorbance were used to investigate the optical properties for the obtained samples, noting important differences regarding the bandgap energy between SPT and RF-MS deposition. In the case of SPT deposited thin films, low optical band gap values from 2.2 to 2.4 eV were obtained whole for the RF-MS films the optical bandgap values were higher ranging from 2.82 eV to 2.90 eV at 70.1 nm. To explain the observed differences, X-ray photoelectron spectroscopy, XPS, was performed, thus obtaining a correlation of the bandgap to the oxidation state of vanadium ions.

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