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Annealing effects on the structural and optical properties of vanadium oxide film obtained by the hot-filament metal oxide deposition technique (HFMOD)

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ABSTRACT

Vanadium oxide films amorphous, nonstoichiometric and highly absorbing in the optical region were deposited on ITO-coated glass and on silicon substrates, by the hot-filament metal oxide deposition technique (HFMOD) and oxidized by *ex-situ* annealing in a furnace at 200, 300, 400 and 500 ºC, under an atmosphere of argon and rarefied oxygen. X-ray diffraction, Raman and Rutherford backscattering spectroscopy as well as optical transmission were employed to characterize the amorphous and annealed films. When annealed at 200 and 300 ºC the as-deposited opaque films become transparent but still amorphous. Under treatments at 400 and 500 ºC a crystalline nonstoichiometric V_2O_5 structure is formed. All the annealed films became semiconducting, with their optical absorption coefficients changing with the annealing temperature. An optical gap of 2.25 eV was measured for the films annealed at 400 and 500 ºC. The annealing in rarefied oxygen atmosphere proved to be a useful and simple ex-situ method to modulate the structural and optical properties of vanadium oxide films deposited by HFMOD technique. This technique could be applied to other amorphous and non-absorbing oxide films, replacing the conventional and sometimes expensive method of modulate desirable film properties by controlling the film deposition parameters. Even more, the HFMOD technique can be an inexpensive alternative to deposit metal oxide films.

Keywords: vanadium oxide film, HFMOD technique, annealing, crystalline structure, optical absorption.

1. INTRODUCTION

Thin films of vanadium oxides find optical applications as an electroactive material for electrodes of electrochromic devices [1], as hole injection material in organic light-emitting diode (OLED) [2], in optical switching and optical memory devices [3], as antireflective coating [4], among others applications. For these devices the vanadium oxide films are usually deposited on ITO-coated slabs, due to its optical transparency and electrical conductivity.

The performance of these optical devices is very dependent on the structure and optical properties of the oxide film [2,3,5]. Thus, by controlling the deposition parameters or performing pos-treatments in the as-deposited films, optimized optical responses can be obtained [3,5,6].

Vanadium oxide films of different composition and properties have been produced by many physical and chemical deposition techniques [1]. However, the deposition of vanadium oxide films by the hot-filament metal oxide deposition technique (HFMOD) is scarcely reported.

The HFMOD is a very simple and inexpensive technique to deposit metal oxide films by heating metal wires of high fusion temperatures, as the transitions metals, in oxygen atmosphere [7]. Thin films of W [8,9,10], Mo [11,12] and V [10] oxides have been produced by this technique, where the electrochromic effect was observed for the W and Mo oxide films [10,12].

In this paper we present the results of structural and optical characterizations of as-grown and pos-annealed thin films of vanadium oxide deposited by the HFMOD technique on ITO-glass substrates. The

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annealing carried out in a mixture of argon and rarefied oxygen atmosphere at 200, 300, 400 and 500 ºC promotes a progressive oxidation of the vanadium film, transforming the amorphous long-range disordered as-deposited vanadium oxide into ordered structures.

The final goal is to show how the crystalline structure and the optical absorption of opaque and amorphous vanadium oxide, obtained by the simple and relatively inexpensive HFMOD technique, is modulated by heat treatments in rarefied oxygen atmosphere in the 200 to 500 ºC range. X-ray diffraction, Raman, Rutherford backscattering and optical spectroscopies were employed as techniques to analyze the evolution in these properties with the annealing temperatures.

2. MATERIALS AND METHODS

Depositions of the vanadium oxide films were undertaken in a stainless-steel chamber maintained at an oxygen pressure of 0.24 Pa by a constant oxygen flow to the chamber, which was continuously pumped by a Roots pump (160 m^3/h) coupled to a rotary pump (10 m^3/h). The chamber pressure was measured using a capacitance manometer and the oxygen flow rate was controlled by an electronic mass flowmeter. A straight 42.0 mm vanadium filament (diameter 1.0 mm) clamped between two electrodes was heated by a 22.0 A electrical current from an AC power supply. Films are formed by the HFMOD process from VO_x gaseous species generated at the filament surface due to thermal reactions between vanadium and oxygen. Description and details of the HFMOD technique are found in literature [7]. The filament temperature, measured during the deposition by an optical pyrometer through a quartz viewport in the chamber wall, ranged from 1365 to 1385 ºC. Indium tin oxide (ITO)-coated glass slides and (100) silicon slabs were used as substrates, and were placed 36 mm below the filament wire, on a water-cooled copper base. Film thicknesses were measured by a high resolution Veeco Dektac3 profilometer.

Oxidation of the vanadium surface wire and its continuum sublimation changes the deposition rate during the processes due to the decreasing in the wire thickness. To monitor the film thickness during the deposition, techniques like quartz crystal sensoring are necessary. When only the deposition time is controlled, different film thicknesses are frequently obtained, as showed in Table 1, for deposition of 30 minutes each. The order in the film deposition sequence was from the thickest to thinnest.

The as-deposited vanadium oxide films were then thermally treated under argon and rarefied oxygen flow in a quartz furnace, at temperatures of 200, 300, 400 and 500 ºC for 1.5 hours each.

Grazing incidence angle X-ray diffraction (GAXRD) was used to investigate the crystalline structure of the films, using the monochromatic Cu-Kα radiation at 0.15406 nm from a Phillips X'Pert X-ray diffractometer.

Raman spectra were acquired at room temperature, in backscattering geometry, using a Jobin-Yvon T-64000 system fitted with a cryogenically cooled (LN_2) Si CCD. The 487.99 nm line of an argon laser was used for optical excitation. A 50x objective lens was used to focus the laser light onto the sample surface to a spot size of 2 μm. The resolution was 1.0 cm^{-1}.

Elemental composition analyses of the films were carried out using Rutherford backscattering spectroscopy (RBS). A beam of singly ionized 2.4 MeV helium atoms aligned normal to the film surface was used with detection at 7° off-normal. Single-crystal (100) Si wafers were used as substrates. The RUMP computational program [13] was applied to the RBS data to obtain the O/V atomic ratio.

The spectral transmittance, between 350 and 1100 nm, of the as-deposited and thermally-treated films were measured using an optical fiber spectrophotometer (OceanOptics, Chem 2000).

Taking into account the low reflectance of these films in the photon energy range of interest, the optical absorption coefficient, α(λ), was calculated from the spectral transmittance curves using the relation:

$$\alpha(\lambda) = \frac{1}{t} 1n\left(\frac{1}{T}\right) \tag{1}$$

Where t is the film thickness and T is the transmittance at wavelength λ. From equation (1), $\alpha(\lambda)$ is calculated under film thickness normalization.

3. RESULTS

Table 1 shows the thicknesses, the annealing temperatures, the visual appearances and the oxygen to vanadium atomic ratio (O/V) for the as-deposited and heat-treated films.

Table 1: Vanadium oxide films, their thicknesses, annealing temperatures, visual appearances and oxygen to vanadium atomic ratios.

SAMPLE	THICKNESS (Å)	ANNEALING TEMPERATURE (ºC)	VISUAL APPEARANCE	O/V RATIO
A	2000	as-deposited	black	1.96
B	740	200	bluish grey	3.32
C	1200	300	bluish grey	2.71
D	900	400	yellow	2.35
E	660	500	yellow	2.14

The X-ray diffractograms of as-deposited and heat-treated films and of the ITO film coated on the glass substrate are shown in Figure 1. Excluding the diffraction peaks belonging to the ITO X-ray pattern, no other peaks in the as-deposited or even in the annealed films at 200 and 300 ºC are observed. An amorphous structure is thus assigned to them. On the other hand, under annealing at 400 and 500 ºC ordered crystalline structures were formed, since vanadium oxide peaks are observed in the diffractograms. The X-ray spectra reveal lines corresponding to the orthorhombic V_2O_5 polycrystalline lattice, assigned from the (001), (101) and (110) crystalline planes (inset of Figure 1). However, the broad and low intensity diffraction peaks indicate that structural defects remain in the vanadium pentoxide structure, even after the annealing. A c parameter of 4.4 Å is calculated from the (001) peak, in good agreement with the literature values [14].

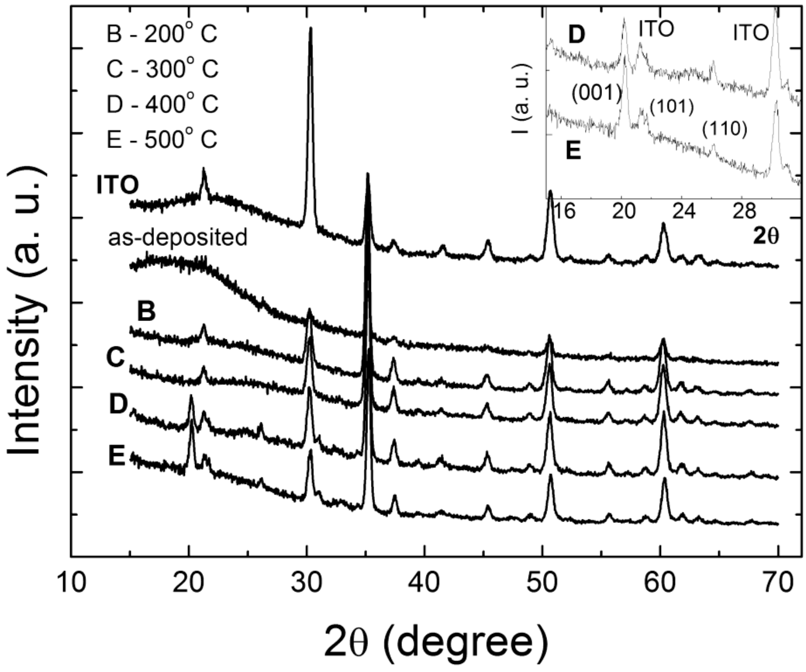

Figure 1: X-ray diffractograms for as-deposited and annealed vanadium oxide films. The inset shows the diffractograms for the D and E polycrystalline vanadium oxides. The diffractograms of the ITO layer X-ray is also shown.

The Raman scattering spectra presented in Figure 2 confirm the amorphous structure for the as-deposited and annealed films at 200 and 300 ºC, as indicated by the X-ray spectra (Figure 1). Under heat treatment at 400 and 500 ºC, well-resolved Raman spectra are observed, with peaks at 104, 146, 198, 285, 305, 406, 483, 528, 702 and 996 cm^{-1}, corresponding to the sequence obtained for V_2O_5 single crystal [15] and polycrystalline vanadium oxide films [16].

The peak at 996 cm^{-1}, superimposed on a plateau around 960 cm^{-1} is attributed to the vanadyl stretching vibrational mode (V-O_V). This plateau belongs to the underlying Si substrate [16] and its intensity decreases with the thickness of the vanadium oxide film, that act as a scattering source for the Si Raman radiation, as can be observed from figure 2. At 702 cm^{-1}, a stretching vibration characterizes the (3V-O_C) bonds. The prominent peak at 146 cm^{-1} is due to the skeleton bending vibration, providing evidence that a layer-like structure was formed by the heat treatments at 400 and 500 ºC, and also suggesting that the polycrystalline V_2O_5 films grow with a preferred orientation about the c-axis perpendicular to the substrate plane, which is in good agreement with the GAXRD measurements.

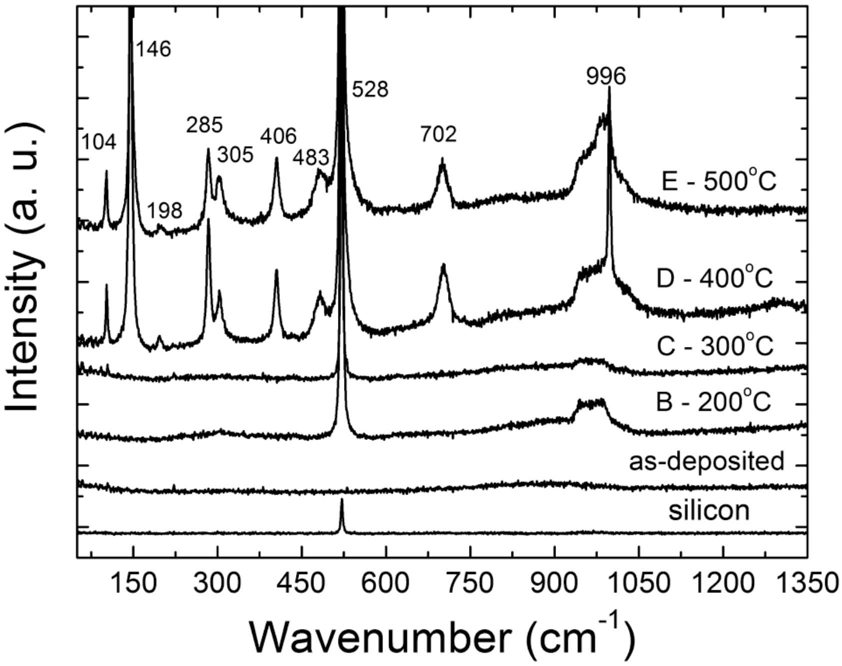

Figure 2: Raman spectra obtained for the as-deposited and thermally treated vanadium oxide films at various temperatures. The spectrum of the (100) silicon substrate is also presented.

Using RBS results was possible to estimate the elemental composition of the samples (data presented on Table 1). The as-deposited films have a low oxygen content (O/V = 1.96), the oxide films thermal treated at 200 (B film) and 300 ºC (C film) presented an excess of oxygen and the polycrystalline D and E films were both nonstoichiometric crystalline vanadium pentoxide, presenting O/V atomic ratio lower than 2.5.

As shown in Table 1 the as-deposited film was visually black, changing to transparent with a bluish grey color under annealing at 200 and 300 ºC, and to a yellow color, characteristic of crystalline vanadium pentoxide, when annealed at 400 and 500 ºC.

Figure 3 shows the optical absorption coefficient α for these films, calculated from equation (1), as function of incident photon energy $h\nu$. The following features can be clearly observed in the figure: (a) A high and featureless optical absorption coefficient, with α ranging from 10^5 to 10^6 cm^{-1} over the whole photon energy range, for the as-deposited films. (b) Under heat treatments at 200 and 300 ºC, both films develop optical absorption coefficients exhibiting similar trends: high and almost constant α values (~5.0 x10^4 cm^{-1}) along an extended energy region ($1.4 < h\nu < 2.7$ eV), followed by a fast increase of α with $h\nu$, in a narrow higher energy region ($h\nu > 2.7$ eV). (c) At the annealing temperatures of 400 and 500 ºC, both oxide films again present similar absorption features, a sharp and increasing optical absorption for $h\nu > 2.5$ eV, in which α grows very fast with photon energy and a lower absorption α in the $1.5 < h\nu < 2.5$ eV energy region. The region where a rapid increase in α with $h\nu$ is observed is characteristic of the fundamental absorption edge in semiconductor materials, resulting of electronic charge transference from the valence to the conduction band. The extended absorption region below about 2.5 eV accounts for transitions related to energy states within the energy band gap, as below explained.

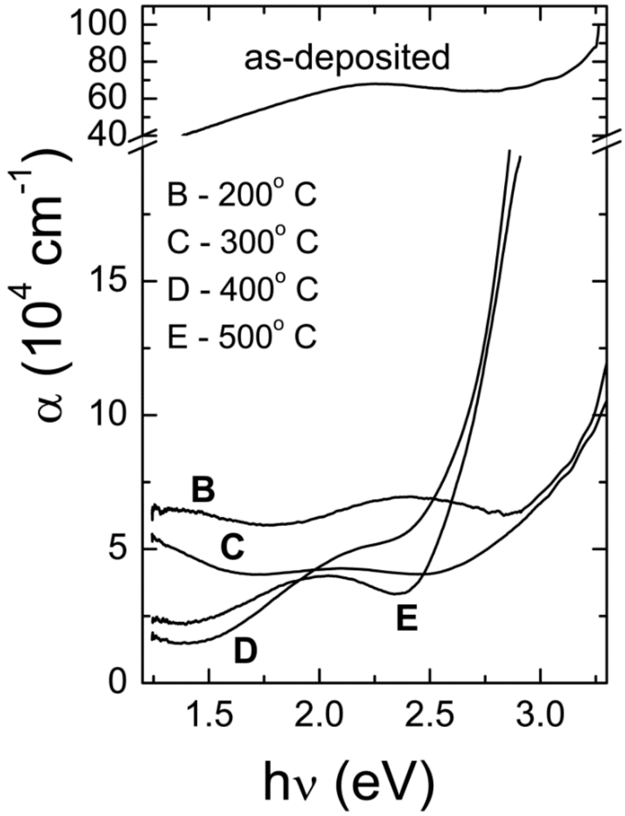

Figure 3: Optical absorption coefficient α as a function of incident photon energy for as-deposited and for thermally-treated vanadium oxide films at various temperatures.

4. DISCUSSION

The crystalline structure of the vanadium pentoxide is well known: at room temperature has an orthorhombic structure [17] with each V atom surrounded by five O atoms which form the corners of a distorted square pyramid, as shown in Figure 4a. The oxygen atoms are designated according to their bonding to the vanadium atoms in the crystal lattice (O_B, O_C and O_A) with the stronger and shortest bond occurring between V and O_A, the oxygen atom at the apex of the pyramid. In the *b*-crystallographic direction, oxygen pyramids pointing alternatively up and down are joined to each other by sharing common edges, forming a zigzag chain, Figure 4b. These chains are linked to each other in the *a*-direction by O_B bridging oxygen atoms, forming layers in the *ab* crystal plane, Figure 4b. The layers are connected to each other by weak bonds between the V atoms of a layer with O_A atoms from the neighbor layer, in the *c* direction. The O_A atoms of the neighbor layers are known as vanadyl oxygen, O_V, when seen coordinated to the V atoms of the considered layer (V-O_V bonds), Figure 4c.

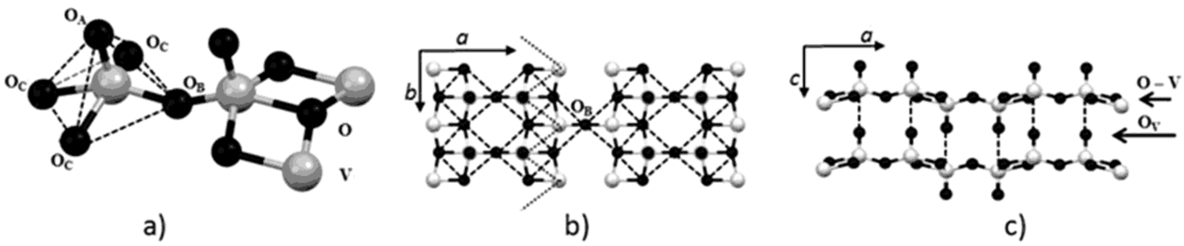

Figure 4: Vanadium coordination in a perfect V_2O_5 lattice (a); projection of the (010) planes of the V_2O_5 lattice, in which the zigzag dotted lines indicate the oxygen pyramids pointing alternatively up (O_A atom visible) and down (V atom visible) in *b* direction (b); projection of the (001) planes (c).

The featureless X-ray diffraction and Raman spectra, resulting from a out of phase X-ray scattering and a lack of vibrational modes, both strongly dependent on the structure and geometry of the crystal, as well as the low O/V atomic ratio of the as-deposited vanadium oxide films, indicate a disordered crystal structure and a highly oxygen deficient oxides, for which a high density of V^{4+} and V^{3+} oxidation states is expected and, consequently, an high optical absorption [18], as was effectively measured, Figure 3. As-deposited films can be considered a nonstoichiometric amorphous VO_2 oxide.

Thermal treatments at 200 and 300 ºC in Ar and rarified O_2 atmosphere does not crystallizes the amorphous as-deposited film that still retains long-range structural disorder, although some local order has occurred. A hypothesis for the high O/V atomic concentration rate for these two films (> 2.5) is the presence of molecular water or oxygen trapped into the disordered and porous as-deposited films during the film deposition or annealing, respectively. However, additional analyses must be performed to support this supposition.

Annealing at 400 and 500 ºC (samples D and E, respectively) desorbs the trapped water and oxygen and structurally reorders the as-deposited amorphous films, as indicated by the X-ray and Raman spectra. The presence of peaks and specially the O vanadyl bond in the Raman spectra at 996 cm^{-1} is a probe of the structural crystallinity for D and E films and its V_2O_5 coordination. However, the V/O atomic ratio lowers than 2.5 indicate nonstoichiometric vanadium pentoxide, with local oxygen vacancies. Vanadium valences of V^{5+}, V^{4+} are expected for both films.

A relevant issue to be noted is the change in the film structure from amorphous to crystalline when the annealing temperature was changed from 300 to 400 ºC. Transitions in structure and composition have been reported for VO_x films as function of atmosphere and annealing temperature [19].

The long and short range disorders occurring respectively, in the amorphous and polycrystalline semiconductor vanadium oxide films, are reflected in the tail and edge shapes of the optical absorption curve, as shown in Figure 3. The absorption tails observed in the annealed films are generated by defects that introduce electronic states into the energy gap, allowing optical absorption for photons with energy lower than 2.5 eV.

The extended and almost constant optical absorption throughout a wide photon energy region and a featureless absorption edges indicate that a high density of energy states was created into the band gap of amorphous B and C films. These defects form an almost continuum of energy states between the valence and conduction bands, centered at 2.38 eV for the film annealed at 200 ºC. Heat treatment at 300 ºC decreases α some more in the tail region, and a more uniform band structure begins to be defined at the absorption edge.

At higher annealing temperatures (400 and 500 ºC) the optical absorption in the tail region present a broad peak at 2.0 eV for the E film, indicating that defect states within the energy band gap are centered in this energy. The inflexion around 2.0 eV in the α curve of the D film indicates that two or more center of defects states are formed into the band gap of this film. A well-defined band structure, however, is now obtained for these polycrystalline vanadium oxide films, as revealed by a sharp absorption edge starting at 2.5 eV.

Optical absorption in low energy region is associated with defect states within the band gap generated by charged V^{+4} and V^{3+} ions [18, 20]. A high concentration of V^{+4} and V^{3+} ions is expected in the amorphous samples B and C, from the general disorder of its bonding. Increasing the annealing temperatures promotes vanadium oxidation and, as consequence, decreasing the relative concentration of V^{+4} and V^{3+} ions and the optical absorptions in the tail region, as observed from Figure 3.

Annealing at higher temperatures, even in a rarefied oxidizing atmosphere, promotes an ordination in the atomic bonds and oxidation of the vanadium cations with partial elimination of V^{+4} states, confirmed by the lower optical absorption in the tail region for D and E samples and by their yellow appearances. The oxidation which occurred during annealing at 400 and 500 ºC establishes the V-O_V bonds, as observed by the presence of the corresponding peaks in the Raman spectra, Figure 2. But part of the O vanadyl vacancies remain in the oxide structure, since a nonstoichiometric O/V < 2.5 ratio was observed from the RBS measurements

The differences in shape and photon energy range of the absorption edge observed between the amorphous (B and C) and polycrystalline (D and E) semiconductor films, Figure 3, can be attributed to the change in the V-O coordination in these two morphologies [18]. In amorphous films B and C, the V atoms are disorderly bonded to O atoms, while for samples D and E, the octahedral V-O coordination is predominant. This explains the great difference in the slope of the absorption edge: whereas a barely defined edge is observed for the amorphous films, clearly identified edges were obtained for the polycrystalline samples.

In semiconductors, the absorption edge has a polynomial dependence on the photon energy, *hν*, which varies with the nature of electronic band-to-band transition. In films with sufficient disorder, as in amorphous and nonstoichiometric polycrystalline films, an indirect allowed transition between the valence and conduction bands is supposed to exist, for which

$$(\alpha h\nu) = B(h\nu - E_o)^2 \qquad (2)$$

Where B is a constant, E_0 is the optical band gap and $h\nu > E_0$ [21]. Theoretical calculation of the band structure and the density of states for V_2O_5 also indicate indirect transitions across the main gap [22].

Figure 5 shows $(\alpha h\nu)^{1/2}$ as function of $h\nu$ for the annealed samples at 400 and 500 ºC. An optical band gap around 2.25 eV was obtained for both D and E polycrystalline samples, in good agreement with those reported for polycrystalline sputtered vanadium pentoxide films [18, 23].

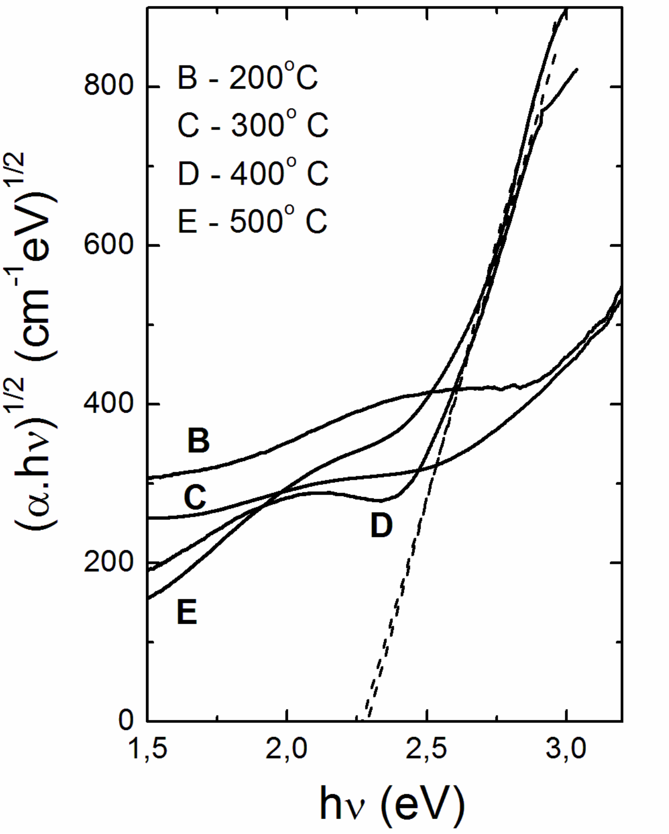

Figure 5: $(\alpha h\nu)^{1/2}$ as a function of incident photon energy for vanadium oxide films annealed at the temperatures indicated in the top left corner. The dashed line is a fit of the linear part of the optical absorption edge for D and E films.

5. CONCLUSION

We have deposited amorphous vanadium dioxide films, oxygen deficient and optically opaque, by the HFMOD technique. Annealing at 200, 300, 400 and 500 ºC in an atmosphere of argon and rarefied oxygen changes the composition, the structure and the optical absorption of the as-deposited film. The films treated at 200 and 300 ºC are still amorphous, but optically transparent. A high optical absorption tail and a broad absorption edge indicate that oxygen vacancies and vanadium in V^{3+} and V^{4+} oxidation states are present in these structurally disordered oxides. When annealed at 400 and 500 ºC a nonstoichiometric polycrystalline vanadium pentoxide is formed in an orthorhombic structure with a well-defined absorption edge for which an optical band gap of 2.25 eV was measured and V^{4+} and V^{5+} oxidation states are supposed to be formed. The *ex-situ* annealing method under controlled argon and oxygen atmospheres showed to be a simple an efficient method to modulate the structure and optical properties of as-deposited amorphous and opaque vanadium oxide films, that can be applied to others metal oxides. The film properties modulate by this method are similar to those obtained by controlling the deposition parameters in traditional vacuum deposition techniques. Both, the HFMOD technique and the ex-situ annealing method can be simple and low cost alternatives for metal oxide thin film processing.

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